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(54) Title: ELECTROLUMINESCENT DEVICE COMPRISING A CHROMOPHORIC POLYMERIC COMPOSITION

(57) Abstract

An electroluminescent device is provided incorporating an emissive layer comprising a processible polymer matrix such as poly(methylmethacrylate) and a chromophoric component such as an asymmetric stilbene or distyrylbenzene. The chromophoric component is blended with the polymer matrix or covalently attached thereto as a side chain and is selected to emit radiation in the region 400 nm to 500 nm when excited to luminesce.

ELECTROLUMINESCENT DEVICE COMPRISING A
CHROMOPHORIC POLYMERIC COMPOSITION

FIELD OF THE INVENTION

This invention relates to semiconductive conjugated polymers
for use in blue light-emitting devices, particularly
electroluminescent devices.

BACKGROUND TO THE INVENTION

In recent years there have been an increasing number of
reports on the use of conjugated molecular materials as the
emissive layers in electroluminescent (EL) devices; C. W. Tang
and S. A. VanSlyke, Appl. Phys. Lett. 1987, 51, 913; C. W.
Tang, S. A. VanSlyke and C. H. Chen, J. Appl. Phys. 1989, 65,
3610; C. Adachi, S. Tokito, T. Tsutsui and S. Saito, Jpn. J.
Appl. Phys. 1988, 27, 59; C. Adachi, T. Tsutsui and S. Saito,
Appl. Phys. Lett. 1989, 55, 1489; C. Adachi, T. Tsutsui and S.
Saito, Appl. Phys. Lett. 1989, 56, 799; M. Nohara, M.
Hasegawa, C. Hosokawa, H. Tokailin and T. Kusomoto, Chem.
Lett. 1990, 189. These materials have efficient light output
and have been shown to be easily amenable to excellent colour
variation.

A considerable number of blue light-emitting molecular
compounds for electroluminescent devices have been
investigated so far. C. Adachi, T. Tsutsui and S. Saito report
a set of examples consisting of anthracene, 9,10-
diphenylanthracene, 1,1,4,4-tetraphenylbutadiene, substituted
distyrylbenzenes, terphenyl, 1,8-naphthalimides, naphthalene-
1,4,5,8-tetracarboximide, 2,5-bis(5-tert-butylbenzoxazol-2-
yl)thiophene, tetraphenylcyclopentadiene,
pentaphenylcyclopentadiene and substituted stilbenes in "Blue
light-emitting organic electroluminescent devices" published
in Appl. Phys. Lett., 1990, 56, 799. Furthermore Eur. Pat.
Appl. EP 319 881, EP 373 582, EP 388 768 (Idemitsu Kosan Co.

Appl. EP 319 881, EP 373 582, EP 388 768 (Idemitsu Kosan Co.
Ltd.) teach that distyrylbenzenes are useful organic compounds
for molecular electroluminescent devices. Green, blue-green
and blue light emission was observed after varying the
substituents on the distyrylbenzene. Other blue light-emitting
compounds are quaterphenyl, as mentioned in Eur. Pat. Appl. EP
387 715 (Idemitsu Kosan Co. Ltd.), and oligothiophenes, as
disclosed in Eur. Pat. Appl. EP 439 627 (Idemitsu Kosan Co.
Ltd.). Recently 1,3,4-oxadiazole dimers have been shown to
give rise to bright blue emission in molecular
electroluminescent devices: Y. Hamada, C. Adachi, T. Tsutsui
and S. Saito, Optoelectronics - Devices and Technologies,
1992, 7, 83 and Y. Hamada, C. Adachi, T. Tsutsui and S. Saito,
Jpn. J. Appl. Phys., 1992, 31, 1812.

However, amorphous films, as obtained by sublimation and used
in all these devices, tend to undergo changes in morphology
due to the heat produced under the device operating
conditions. This results in the breakdown of molecular
electroluminescent devices after longterm storage or even
earlier during continuous driving tests.

Working with electron-transporting layers in association
with electroluminescent devices which have polymeric
light-emitting layers the present applicants found that a
uniform dispersion of tert-butyl-PBD (1) in poly(methyl
methacrylate) (PMMA) could be formed. The results are
reported in "Light-emitting diodes based on conjugated
polymers: Control of colour and efficiency", P.L. Burn,
A.B. Holmes, A. Kraft, A.R. Brown, D.D.C. Bradley and R.H.
Friend in: Electrical, optical, and magnetic properties of
organic solid state materials: symposium held December
2-6, 1991, Boston, Massachusetts, USA, L.Y. Chiang, A.F.
Garito, D.J. Sandman (Eds.), Pittsburgh, 1992, Mat. Res.
Soc. Proc. 1992, 247, 647. Films were obtained by
spin-coating a solution of (1) and PMMA in chloroform and
were found to be stable under the device operating
conditions.

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(1)
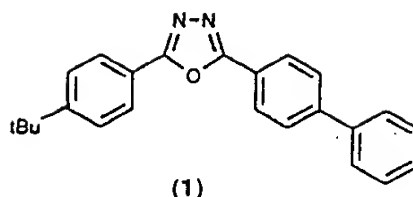
Dispersion-type electroluminescent devices have been reported
in Jpn. Kokai Tokkyo Koho JP 03/147,290 (Hitachi Chemical Co.
Ltd.); Jpn. Kokai Tokkyo Koho JP 03/119,090 (NEC Corp.); Jpn.
Kokai Tokkyo Koho JP 03/250,582 (Hitachi Maxell Ltd.); US
5,075,172 (Cape Cod Research Inc.). "Molecularly doped
polymers as a hole transport layer in organic
electroluminescent devices" teaches the application of a
dispersion of N, N'-diphenyl-N,N'-bis(3-methylphenyl)benzidine
in polycarbonate as the hole transport layer and tris(8-
quinolinato)aluminium as the emitting layer and is published
by J. Kido, K. Hongawa, M. Kohda, K. Nagai, K. Okuyama, Jpn.
J. Appl. Phys., 1992, 31, L960. "A light-emitting diode using
as recombination layer a blend containing a poly(para-
phenylene vinylene) oligomer" has been disclosed by W.
Tachelet and H. J. Geise at the International Conference on

Science and Technology of Synthetic Metals in Gothenburg,
Sweden (August 12-18, 1992). A light-emitting diode has been
constructed using 1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]-
2,5-dimethoxybenzene blended in polystyrene as the light-
emitting layer. According to the authors the advantage of such
a blend over a pure oligomer was seen in a combination of
mechanical and electro-optical properties which was not easily
attainable with the presently known pure electro-active
compounds.

Currently the patent literature contains only occasional
reports on the use of potential electroluminescent dyes which
are attached to a polymer in form of a side chain. Eur. Pat.
Appl. EP 390 551 (Kabushiki Kaishi Toshiba) discloses a way of
introducing light-emitting organic dyes in the repeating unit
of main and side chain oligomers with standard linking units.

Recently a number of patents appeared dealing with using
polymers as luminescent substances in organic EL devices.
Example of such polymers are poly(vinylanthracene), Jpn. Kokai
Tokkyo Koho JP 03/020 992 and 03/037 991 (Seiko Epson Corp.),
and poly(vinylanthracene)/poly(styrene) copolymers, Jpn. Kokai
Tokkyo Koho JP 03/002 209 (Idemitsu Kosan Co. Ltd.); it should
be noted that during radical polymerisation of vinylanthracene
the anthracene ring system does not stay intact and the
aromatic ring is not a side chain in the final polymer but is
incorporated into the main chain. Ferroelectric liquid
crystalline poly(methacrylate)s have been disclosed as
dispersants for light-emitting substances, such as perylene,
Jpn. Kokai Tokkyo Koho JP 03/043 991 (Canon KK). Polymers of
type $(-Ar-O-C_6H_4-CH(Ar')-C_6H_4-O-)_n$, Jpn. Kokai Tokkyo Koho JP
03/163 185 (Idemitsu Kosan Co. Ltd.), and (co)polymers of
vinyl compound monomers having aromatic substituents, Jpn.
Kokai Tokkyo Koho JP 03/137 186 (Asahi Chemical Ind. Co.
Ltd.), are further examples of prior art.

Conjugated blue light-emitting polymers have also been
disclosed. "Synthesis of a segmented conjugated polymer chain
giving a blue-shifted electroluminescence and improved
efficiency" by P. L. Burn, A. B. Holmes, A. Kraft, D. D. C.
Bradley, A. R. Brown and R. H. Friend, J. Chem. Soc., Chem.
Commun., 1992, 32 described the preparation of a light-
emitting polymer that had conjugated and non-conjugated
sequences in the main chain and exhibited blue-green

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electroluminescence with an emission maximum at 508 nm. Blue
light-emission was observed in two other conjugated polymers.
Poly(p-phenylene) sandwiched between indium-tin oxide and
aluminium contacts has been published by G. Grem, G. Leditzky,
B. Ullrich and G. Leising in Adv. Mater., 1992, 4, 36.
Similarly, Y. Ohmori, M. Uchida, K. Muro and K. Yoshino
reported on "Blue electroluminescent diodes utilizing
poly(alkylfluorene)" in Jpn. J. Appl. Phys., 1991, 30, L1941.

Although there are already reports of limited and highly
specialised prior art, there is still a need for
electroluminescent polymers with a chemically tunable blue
light emission.

Summary of the Invention

The present invention provides an electroluminescent
device incorporating an emissive layer comprising a
processible polymer matrix and a chromophoric component,
wherein the chromophoric component is blended with the
polymer matrix or covalently attached thereto as a side
chain and is selected to emit radiation in the region
400nm to 500nm when excited to luminesce. Compositions
are also provided which comprise the processible polymer
matrix and the chromophoric component.

A typical electroluminescent device is described in
further detail in International Patent Publication No. WO
90/13148 and comprises a semiconductor layer generally in
the form of a thin dense polymer film comprising at least
one conjugated polymer. A first contact layer is in
contact with a first surface of the semiconductor layer
and a second contact layer is in contact with a second

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surface of the semiconductor layer. Typically, the polymer film of the semiconductor layer has a sufficiently low concentration of extrinsic charge carriers that, on applying an electric field between the first and second contact layers across the semiconductor layer so as to render the second contact layer positive relative to the first contact layer, charge carriers are injected into the semiconductor layer and radiation is emitted from the semiconductor layer.

The region 400nm to 500nm broadly defines the blue light region for emission. Preferably, the chromophoric component is selected to emit radiation in the region 430nm to 480nm, more preferably around 450nm. As a precondition to electroluminescent emission in the blue light region, the chromophoric component should exhibit fluorescence in the selected wavelength range.

Advantageously, the chromophoric component has the general formula Ar_1-Ar_2 or $Ar_1-Ar_2-Ar_3$ in which Ar_1, Ar_2 and Ar_3 are the same or different, each representing an aromatic group. By aromatic group is meant all types of aromatic groups including heteroaromatics, as well as aromatics incorporating more than one ring structure, including fused ring structures. The aromatic groups are conjugatively linked together, for example by a double bond. Advantageously, the double bond has a <u>trans</u> conformation. This is found to be advantageous because <u>cis</u>-stilbene has a much lower fluorescence quantum yield than <u>trans</u>-stilbene, and this is expected to extend to other materials as well.

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In a preferred embodiment, the chromophoric compound is asymmetric in order to improve the solubility of the chromophoric compound in both the polymer matrix and in the medium used for processing. Asymmetry may be introduced into the chromophoric compound either by the nature of the aromatic groups or by the incorporation of one or more substituents on the ring of at least one of the aromatic groups. For example, a heteroaromatic group may be chosen as one of the aromatic groups in which the heteroatom is such that asymmetry is introduced into the chromophoric component. Advantageously, one or more of the aromatic groups is substituted with a solubilizing group. The solubilizing group may render the chromophoric component soluble in both the polymer matrix and in the medium used for processing. This is particularly useful where the chromophoric component is blended with the polymer matrix.

Most preferably, the chromophoric component comprises a stilbene or a distyrylbenzene. Various substituents may be incorporated on the ring of the Ar_1 moiety of the stilbene or distyrylbenzene to render the molecule asymmetric. Whilst 2,5 substitution using a t-butyl group and a methoxy group as substituents has been found to work well (see the Examples which follow), various other substituents may be used with these and other chromophoric components. For example, long chain solubilizing groups such as alkoxy, aryl, alkyl or polycyclic groups may be used, preferably with a chain length in the range C_4 to C_{22}.

Where the chromophoric component is covalently attached to the polymer matrix, it is advantageous to use a non-conjugated spacer between the polymer matrix and the

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chromophoric component. The spacer preferably comprises a carbon chain of at least two carbon atoms, more preferably around 6 carbon atoms. Use of the spacer normally gives the advantage of improved processibility and solubility.

In this embodiment, it is preferred that the polymer matrix comprises a poly(methylmethacrylate). Poly(arylene-1,2-ethanediyl) copolymers may also be used as the polymer matrix.

In a further embodiment of the present invention, the chromophoric component forms at least part of a chromophoric polymer and is blended with the polymer matrix. Preferably, the chromophoric polymer comprises a poly(paraphenylene). It may also be advantageous to include in the blend of chromophoric polymer and matrix polymer an electron transfer agent to help in transferring electrons to the chromophoric polymer. Such electron transfer agents include oxadiazoles, triazoles and other aromatic compounds or polymers having a high electron affinity.

Preferably, the poly(paraphenylene) has the general formula I:
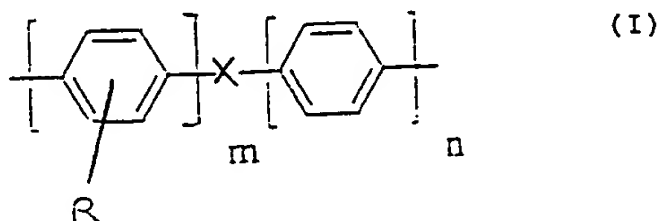
(I)

in which m is an integer and n is an integer or zero, and R represents up to four solubilizing groups. X is optionally present in the polymer and is a non-conjugated spacer, such as defined above. Advantageously, the poly(paraphenylene) has the general formula (II):
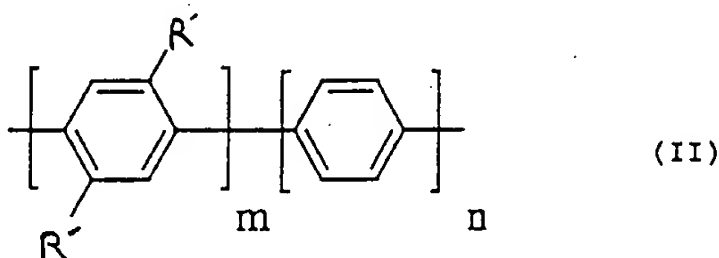
(II)

in which R' represents an alkyl or alkoxy group. More preferably, R' represents $C_6H_{13}O$ and either m is an integer and n is zero or m:n = 2:1.

Whether the chromophoric component comprises a small molecule or a part of a chromophoric polymer, the polymer matrix preferably comprises poly(methylmethacrylate), poly carbonate or polystyrene.

In a further aspect, the present invention provides an electroluminescent device incorporating an emissive layer comprising a processible polymer matrix and a chromophoric

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component, in which the chromophoric component is in the main chain of the polymer matrix and is selected to emit radiation in the region 400nm to 500nm when excited to luminesce, wherein the chromophoric component comprises a stilbene or distyrylbenzene moiety.

Preferably, the stilbene or distyrylbenzene moiety includes a non-conjugated spacer region as part of the polymer main chain so as to interupt the conjugation in the polymer main chain. The stilbene or distyrylbenzene moiety may be substituted as discussed above.

In a further aspect, the present invention provides an electroluminescent device incorporating an emissive layer comprising a processible polymer which comprises a polymeric chromophoric component of general formula (I), as described above, in which m is an integer, n is an integer or zero and R represents up to four solubilizing groups. The polymeric chromophoric component is selected to emit radiation in the region 400nm to 500nm when excited to luminesce. Preferably, the polymeric chromophoric component comprises the polymer of general formula II, as described above, in which R' represents an alkyl or alkoxy group. More preferably, R' represents $C_6H_{13}O$ and either m is an integer and n is zero or m:n = 2:1. In one embodiment, the polymer may be blended with an electron transfer agent, such as PBD. Alternatively, the polymer can form the emissive layer adjacent a polymeric hole transport layer, such as PPV.

The first approach in this investigation was to form a
dispersion of stilbene in PMMA. From theoretical
considerations it is known that at least 30 % of the
dispersion has to be the active chromophore. The device also
requires the formed film to be clear with no crystallites at
all or, alternatively, with an even distribution of
crystallites. This could not be achieved with stilbene in
PMMA. A range of concentrations of stilbene in PMMA was
investigated, but it was not possible to form films without
crystallites of the required thickness for a device by spin-
coating from chloroform.

Comparison of stilbene with (1) showed several important
differences. First, stilbene has a high degree of symmetry
compared with (1) which gives it a greater tendency of packing
and thus promotes the formation of crystallites. Second, (1)
has a large lipophilic tert-butyl group which makes it more
compatible with PMMA and which is not present in stilbene.
Finally, the tert-butyl group on (1) decreases the ability of
the molecules to stack closely together. Therefore it was
decided to develop a stilbene (2) with decreased symmetry and
a solubilising tert-butyl group.
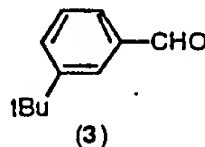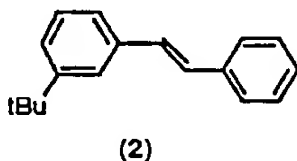
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However, the required aldehyde (3) could not be easily
obtained from commercially available starting materials and
therefore it was decided to synthesise stilbene (4) (Scheme
1). The first step consisted of a Friedel-Crafts alkylation of
o-anisaldehyde using aluminium chloride and tert-
butylchloride.
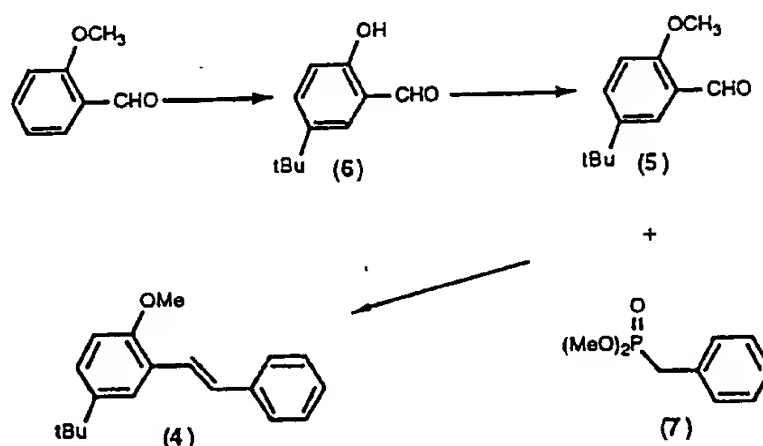
Scheme 1

Under these conditions the aldehyde (6) was obtained in 40 %
yield. This is the result of a demethylation reaction caused
by the alumininium chloride in an analogous fashion to that
which can be achieved with boron trichloride. The aldehyde (5)
was prepared from (6), tetra-n-butylammonium hydroxide and
methyl iodide in dimethylformamide (DMF). The aldehyde (5) was
coupled with the phosphonate (7) using sodium hydride as base
in DMF. The stilbene (4) was isolated in 71 % yield. The
absorption spectrum of stilbene (4) is shown in Figure 1.

Evaluation of (4) as a dispersion in PMMA in an
electroluminescent device (Example 1) showed two important
points. First, emission was achieved in the violet region, and
second, the stability of the devices was not high. Such lack
of stability appeared to be due to the poor quality films
formed by spin-coating of the dispersion from a chloroform

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solution which we attribute to the mobility of the stilbene
and its ability to trap solvent. The current-voltage
characteristics (Figure 2) indicate a turn-on voltage of ca. 8
V for a device having a 100 nm thick light-emitting layer. The
luminance of a test device was fairly proportional to the
current as shown by Figure 3.

To improve the performance it was decided to synthesise
distyrylbenzene (8) (Scheme 2) which should give emission at a
longer wavelength, be a solid and have the required lack of
symmetry and the necessary polymer compatibility. The first
step in the synthesis of (8) was the reduction of (5) with
lithium aluminium hydride under standard conditions to give
the alcohol (9) in 82 % yield. The alcohol (9), dissolved in
1,4-dioxane, was treated with concentrated hydrochloric acid
to yield (10) in 89 % yield. The chloride (10) was converted
into the phosphonate (11) in 55 % yield by treatment with
trimethyl phosphite at reflux. The phosphonate (11) was
coupled with 4-stilbenecarbaldehyde (12) under the same
conditions used to form (4) and the distyrylbenzene (8) was
isolated in 73 % yield.

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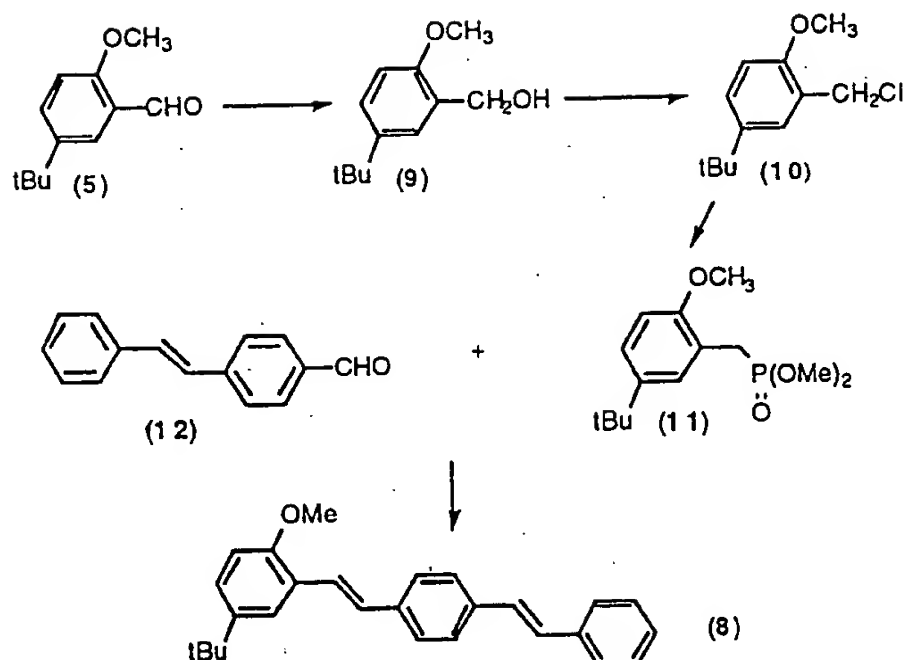
Scheme 2

Evaluation of a dispersion of (8) in PMMA in an
electroluminescent device showed that the emission was indeed
blue (Example 2). The films formed by spin-coating from a
chloroform solution were still not of the required quality.
However, dispersions of (8) in crosslinked PMMA formed high
quality uniform films when spun from chloroform solutions and
these have been evaluated in electroluminescent devices. The
absorption spectrum of (8) is shown in Figure 4. For
comparison its photoluminescence (PL) spectrum can be seen in
Figure 5. Figure 6 shows that the average electroluminescence
spectrum is comparable to the average photoluminescence
spectrum. The current-voltage characteristics (Figure 7)
indicate a turn-on voltage of ca. 20 V for an
electroluminescent layer of 250 nm thickness. The luminance of
a test device was fairly proportional to the current (Figure
8).

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A much more stable and efficient device was constructed using polystyrene as the binder (50% w/w). This showed efficiencies of over 1% with a turn-on voltage of 15 V (figure 14).

From this work we have shown that it is possible to achieve electroluminescence from a molecular conjugated unit in a polymer binder by judicious design of the chromophore. In doing so we have defined some of the parameters of the active chromophore. The experience gained from the design of molecular blue light-emitting dyes which were dispersed in a blend with PMMA and used in EL devices was now applied to the design of suitably substituted side chain polymers. It is long known from work on polymers which exhibit second order susceptibilities, $\chi^{(2)}$, that dyes can be attached as side chains on a poly(methacrylate). For practical reasons the aromatic substituents, which for $\chi^{(2)}$ systems are of push-pull type, cannot be directly linked to the ester group in methacrylate. A spacer is usually inserted in between to improve solubility and processability of the final polymer. Although such polymers are known for applications in non-linear optics, the idea of designing electroluminescent polymers with fluorescent side-chains is new. Our strategy involved a suitably substituted stilbene or distyrylbenzene with a flexible spacer being connected to methacrylate and being polymerised. We aimed to apply such fluorescent polymers as blue light-emitting layers in electroluminescent devices.

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Our first example of an electroluminescent polymer was a poly(methacrylate) with a stilbene side chain. Stilbene itself would not be of much use because its fluorescence emission maximum is expected to be in the ultraviolet. Three alkoxy substituents were incorporated to shift it towards the visible part of the spectrum. The substitution pattern (2',5',4) was chosen to ensure lack of symmetry in the stilbene which usually results in increased solubility of the molecular compounds and the final polymer. The synthesis was straight forward as outlined by Scheme 3.
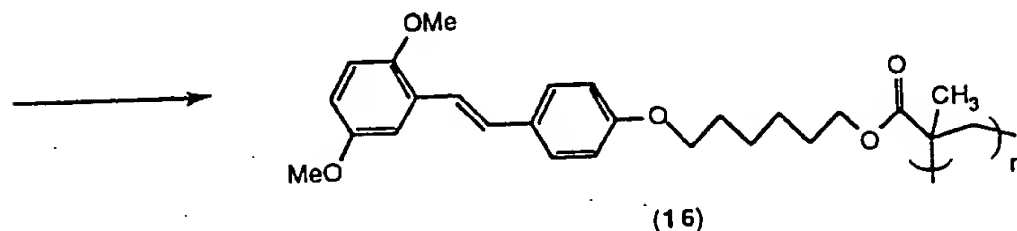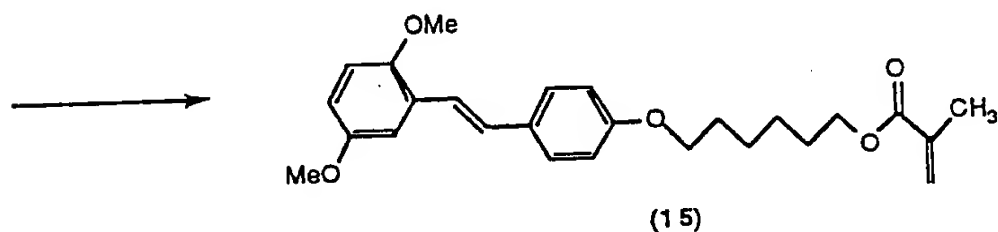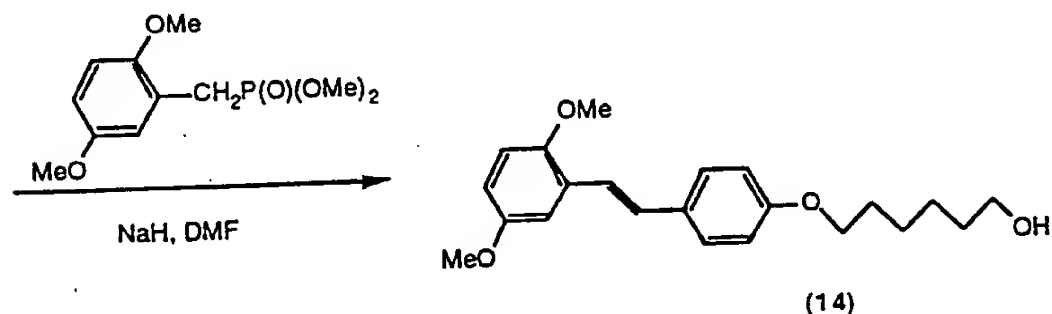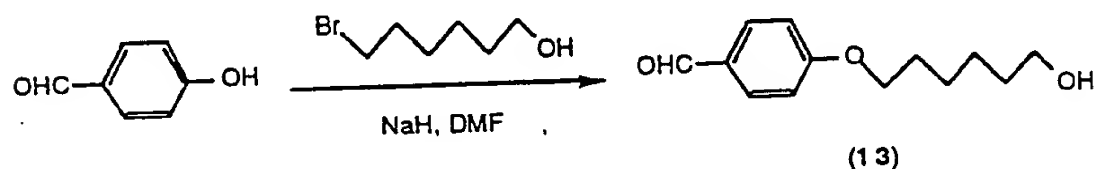
Scheme 3

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The known aldehyde (13) was obtained from p-
hydroxybenzaldehyde and 6-bromohexane in 45 % yield. A Wittig-
Horner reaction with dimethyl 2,5-dimethoxybenzylphosphonate
then furnished the alcohol (14) in 47 % yield which functioned
as the fluorescent dye already connected to a flexible
hexamethylene spacer group. Esterification with methacryloyl
chloride gave the monomer (15). Radical polymerisation then
yielded a substituted poly(methacrylate) (16) which was
purified by reprecipitation.

The film forming properties of polymer (16) were good. It was
successfully tested as a light-emitting polymer in an
electroluminescent device (Example 3). Devices were however
short-lived and the light output faded away rather rapidly.
Despite the bathochromic substituents the emitted light was
violet as expected from the model compound studies.

To shift the fluorescence maximum to longer wavelengths, the
conjugated system was extended in a second attempt to a
distyrylbenzene system which was shown in our model compound
studies to exhibit blue fluorescence. This time one methoxy
group on the aromatic system was substituted by a tert-butyl
group to act as a solubilising group. The synthesis is
outlined in Scheme 4.

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Scheme 4

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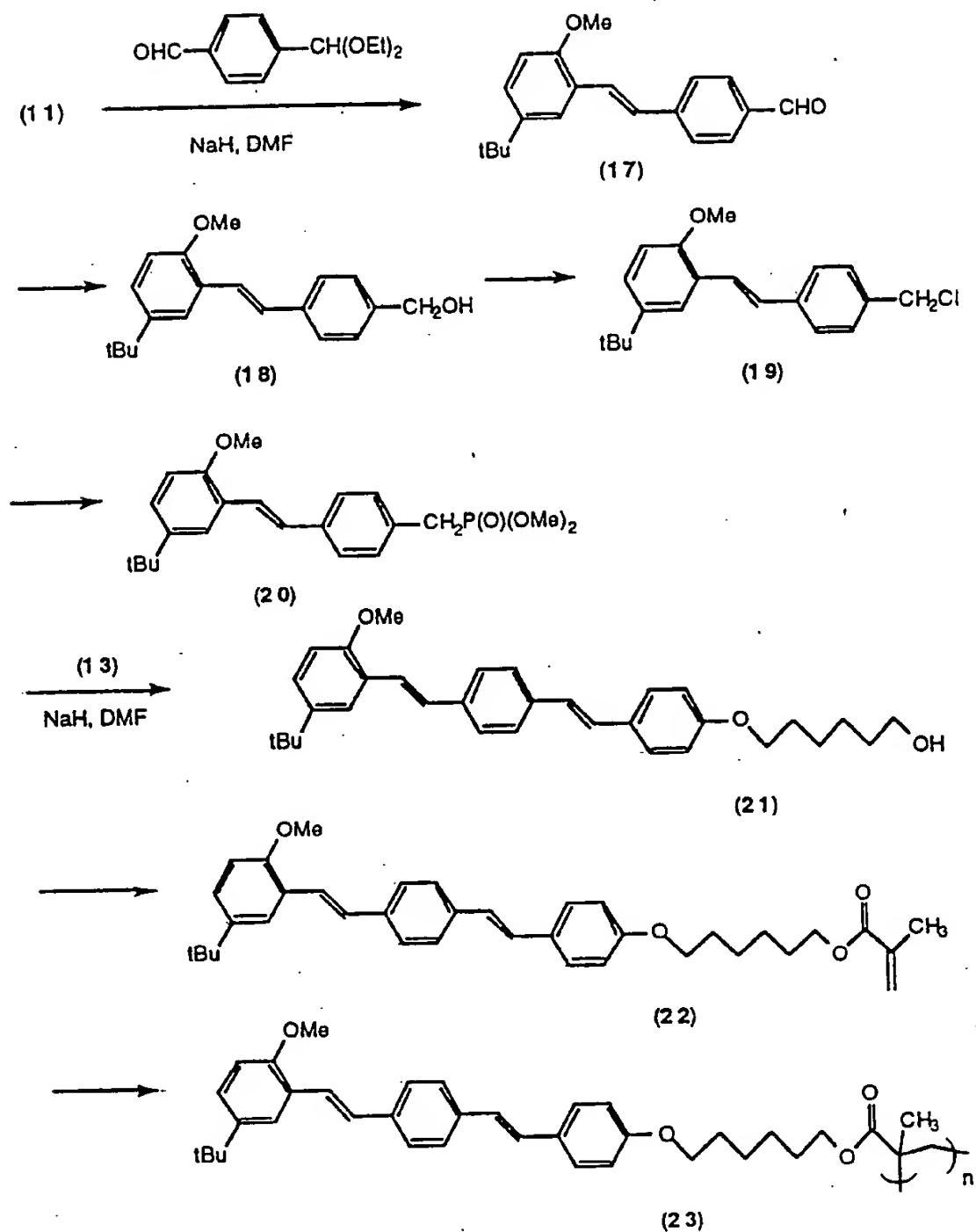
The extension of the conjugated system was achieved as before
by Wittig-Horner type chemistry. Hence, phosphonate (11) and
terephthaldehyde mono(diethyl acetal) gave aldehyde (17) in 69
% yield. Subsequently, the aldehyde was reduced, the alcohol
obtained transformed to the chloride and the chloride reacted
with trimethyl phosphite to give phosphonate (20) in 21 %
overall yield. Coupling with (13) furnished alcohol (21)
which was esterified with methacryloyl chloride.
Polymerisation of monomer (22) was again conducted in toluene
using a radical initiator (AIBN). This resulted in polymer
(23) which fluoresced blue both in solution and in the solid
state. The polymer was separated into two fractions by
fractionated precipitation with ether/dichloromethane. The
more soluble fraction proved to have an appreciable nitrogen
content (0.27 %) originating from the AIBN initiator and
indicated a moderate molecular weight. The remaining fraction
was too insoluble to be of any use. The absorption spectrum
of (23) (Figure 9) was almost identical to distyrylbenzene
(8) (Figure 4).

Polymer (23) exhibited blue fluorescence in the solid state
and was used as the light-emitting layer in an
electroluminescent device (Example 4). An ITO/polymer/calcium
device showed a blue-violet light emission which decayed
rapidly. The quantum efficiency of a test device was ca. 0.007
%. The current-voltage characteristics (Figure 10) indicate a
turn-on voltage of ca. 30 V for an electroluminescent layer of
300 nm thickness. The luminance of a test device was again
fairly proportional to the current (Figure 11).

Another route to a blue emitting polymer involves
incorporation of the chromophore into the polymer main chain.
Prior art for polymers of this type is "New thermotropic
polyesters from distyrylbenzene bisphenols" by T. E. Mates and
C. K. Ober, J. Polym. Sci., Polym. Lett., 1990, 28, 331. The

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authors describe the synthesis of such a polymer and
anticipate applications in nonlinear optics, however, not in
electroluminescence. A similar fluorescent distyrylanthracene
main chain polyester with liquid crystalline behaviour has
been disclosed in Jpn. Kokai Tokkyo Koho JP 02/117,915
(Mitsubishi Petrochemicals). The only example so far of an
electroluminescent main chain nonconjugated polymer has been
reported by C. Hosokawa, N. Kawasaki, S. Sakamoto and T.
Kusumoto in *Bright blue electroluminescence from hole
transporting polycarbonate* in Appl. Phys. Lett. 1992, 61,
2503. Purplish blue light emission was observed from a 4,4'-
diphenylaminostilbene chromophore in a polycarbonate main
chain polymer.

Benzene-1,4-dimethanol was mono-silylated to give alcohol
(24). Swern oxidation yielded aldehyde (25) which was
converted to disilyl-protected distyrylbenzene (27) by Wittig
reaction using bis-phosphonium salt (26). Deprotection was
achieved with tetra-n-butylammonium fluoride. Diol (28) was
reacted with redistilled sebacoyl chloride to give polymer
(29) which was purified by precipitation into hexane and into
methanol. Elemental analysis and NMR spectra suggested that
the material prepared was an oligomer with ca. six repeating
units (Example 5). Much higher molecular weights are likely to
be obtained under slightly different polymerisation
conditions. The solution absorption spectrum of polymer (29)
is shown in Figure 12. The photoluminescence spectrum of
polymer (29) varied from blue in dilute solution to blue-
green in a thin film. The large Stokes shift suggests that the
chromophore groups interacted significantly in the solid
state. This might be counteracted by the addition of bulky
substitutents on the phenylene rings. As the melting point of
the polymer was over 90 °C, it was possible to test it in an
electroluminescent device. The electroluminescent device
efficiency was about 0.01 %. The light output faded rapidly,
though recovered on resting the device.

$$HOCH_2 \text{—} \langle \text{benzene ring} \rangle \text{—} CH_2OH \xrightarrow[\text{2) tBuMe}_2\text{SiCl}]{\text{1) NaH, THF}} HOCH_2 \text{—} \langle \text{benzene ring} \rangle \text{—} CH_2OSiMe_2tBu$$

(24)

$$\xrightarrow[\text{2) NEt}_3]{\text{1) (COCl)}_2, \text{ DMSO, CH}_2\text{Cl}_2} OHC \text{—} \langle \text{benzene ring} \rangle \text{—} CH_2OSiMe_2tBu$$

(25)

Cl⁻ Ph₃P⁺CH₂— (benzene ring with OMe and MeO) —CH₂PPh₃⁺ Cl⁻ $\xrightarrow[\text{(25)}]{\text{NaOEt, EtOH}}$

(26)

tBuMe₂SiOCH₂— (stilbene system with OMe, MeO) —CH₂OSitBuMe₂ $\xrightarrow[\text{THF, CH}_2\text{Cl}_2]{\text{NBu}_4\text{F}}$

(27)

HOCH₂— (stilbene system with OMe, MeO) —CH₂OH + Cl—CO—(CH₂)₈—CO—Cl $\xrightarrow{\text{pyridine}}$

(28)

$$\left[OCH_2 \text{—} \langle \text{stilbene system with OMe, MeO} \rangle \text{—} CH_2O\text{-CO-}(CH_2)_8\text{-CO} \right]_n$$

(29)

Scheme 5

J. M. Machado, F. R. Denton, J. B. Schlenoff, F. E. Karasz and
P. M. Lahti have shown in "Analytical methods for molecular
weight determination of poly(p-xylylidene dialkyl sulfonium
halide): degree of polymerisation of poly(p-phenylene
vinylene) precursors", J. Polym. Sci., Polym. Phys., 1989, 27,
199 that sodium thiophenolate completely substitutes sulfonium
groups in the tetrahydrothiophenium precursor polymer to PPV,
(30), to furnish a polymer (31) which is soluble in
chlorinated solvents. Similar observations have been made by
R. A. Wessling and R. G. Zimmerman (Dow Chemical Co.), US
3,404,132. Their disclosure also describes that the resulting
polymer shows intense blue fluorescence. We repeated the
results (Scheme 6) and confirmed the observation. However, the
polymer (31) failed to produce electroluminescence in a
standard EL device likely due to insufficient conjugation.
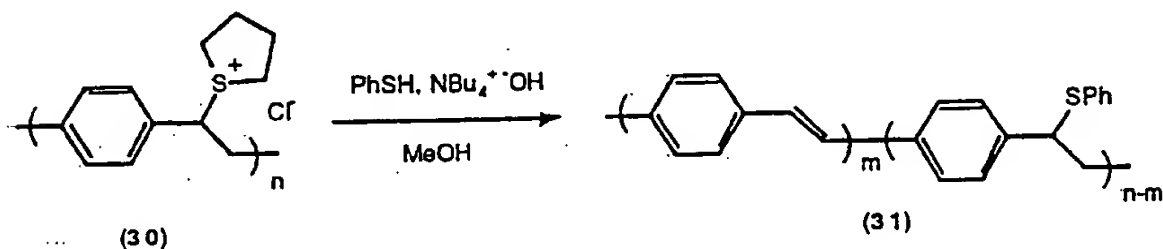
Scheme 6

That thiolates can react as modifier groups with precursor
polymers to PPV is also disclosed in PCT/WO92/03490 and in
PCT/WO92/03490. What is not anticipated, however, is the
possibility that the thiolate can itself be a fluorescent dye.
This would permit the preparation of a novel class of side-
chain polymers.

The following scheme shows examples which form part of this
invention.
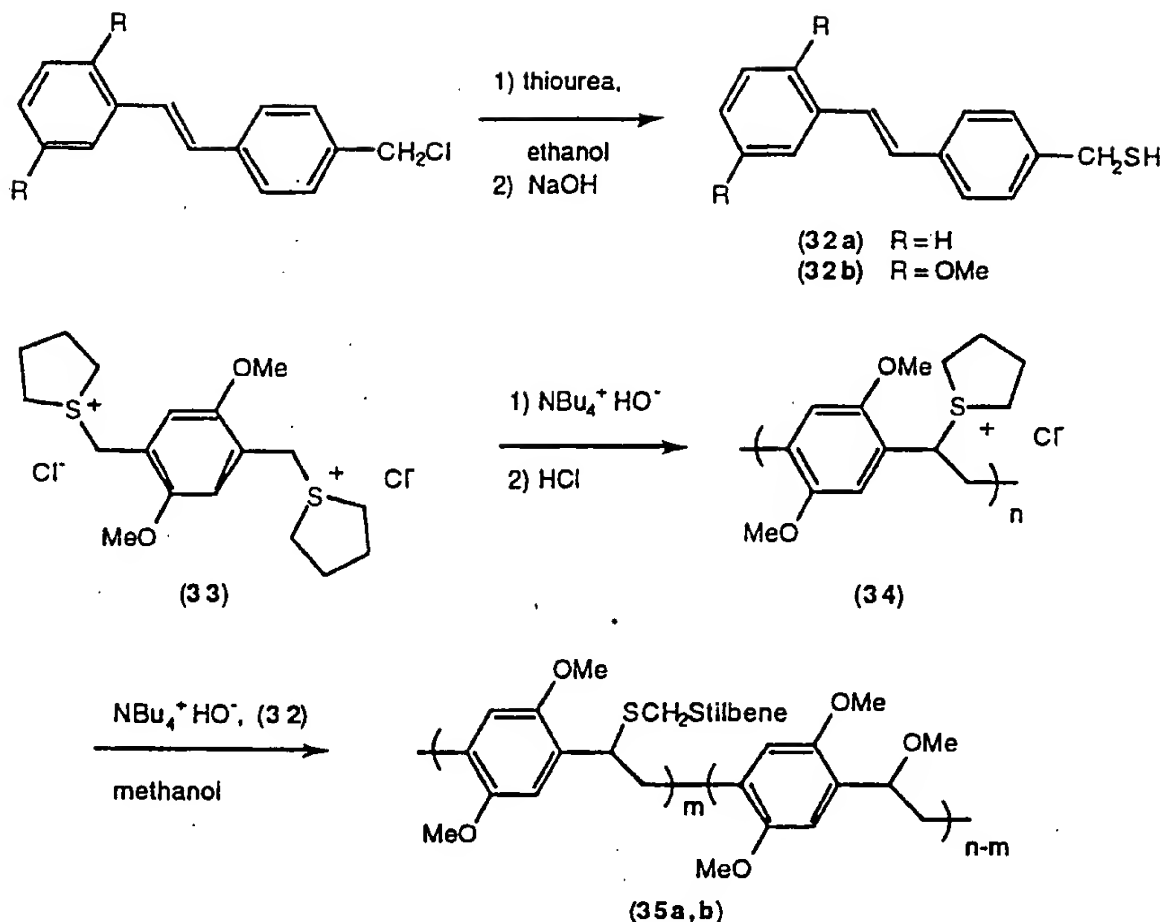
Scheme 7

Thiols (32a,b) were prepared by a standard procedure. Bis-
sulfonium salt (33) was polymerised with tetra-n-butylammonium
hydroxide in methanol to give the sulfonium precursor polymer
to poly(2,5-dimethoxy-p-phenylenevinylene), (34). A solution
of equimolar amounts of base and thiol (32a) or (32b),
respectively, was then added resulting in two polymers
(35a,b) which contained the fluorescent stilbene as a side
chain (Examples 7-8). An ^{1}H NMR spectrum of the polymer
obtained from (32b) indicated that only 15-25 % of the
stilbene was incorporated. IR, UV, and photoluminescence
experiments were carried out showing that the stilbene was in
fact present. No electroluminescence was observed presumably

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due to the low concentration of electroactive species. This is again in accordance to our statement on p. 2 emphasising that theoretically at least 30 % of the active chromophore in the polymer binder are necessary. The low percentage obtained in the above case is basically due to the fact that the highly reactive sulfonium precursor polymer to poly(2,5-dimethoxy-p-phenylenevinylene) had been used.

Instead the sulfonium precursor polymer to PPV (36) was employed, which allowed much better control of the substitution reaction (scheme 8, figure 18). The resulting polymer (37) showed blue fluorescence in solution.

Another class of polymers that show promise for blue emission is the poly(p-phenylenes). The insoluble, unsubstituted poly(p-phenylene) has been shown to luminesce in the blue region as described previously. Soluble versions were prepared via palladium-catalysed coupling reactions (scheme 9, figure 18). These new new polymers showed good blue fluorescence and were used in a variety of EL devices. A device using a blend of polymer (41) in polystyrene in a configuration ITO/polymer blend/Ca had an excellent efficiency of ca. 1 % although the driving voltage was high (70-90V). By using more of the phenylene polymer in the blend and employing a bilayer structure (ITO / PPV/ polymer blend/ Ca) the driving voltage could be reduced to 50V, although the PPV layer absorbed some light. A 1:1 mixture of the polymer (42) with the oxadiazole (43) resulted in much lower driving voltages (10 V) but the device decayed rapidly.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the absorption spectrum of 2-methoxy-5-tert-butylstilbene (4).

Figure 2 is a graph showing the current/voltage characteristics of a thin film of 2-methoxy-5-tert-butylstilbene (4) and PMMA.

Figure 3 is a graph showing the luminance/voltage characteristics of a thin film of 2-methoxy-5-tert-butylstilbene (4) and PMMA.

Figure 4 shows the absorption spectrum of 2-methoxy-5-tert-butyldistyrylbenzene (8) and of polymer (23).

Figure 5 is a graph showing the absorption and the photoluminescence spectrum of 2-methoxy-5-tert-butyldistyrylbenzene (8).

Figure 6 is a graph showing the average photoluminescence and the average electroluminescence spectrum of a thin film of 2-methoxy-5-tert-butyldistyrylbenzene (8) and PMMA.

Figure 7 is a graph showing the current/voltage characteristics of a thin film of 2-methoxy-5-tert-butyldistyrylbenzene (8) and PMMA.

Figure 8 is a graph showing the luminance/voltage characteristics of a thin film of 2-methoxy-5-tert-butyldistyrylbenzene (8) and PMMA.

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Figure 9 shows the absorption spectrum of polymer (23).

Figure 10 is a graph showing the current/voltage characteristics of a thin film of polymer (23).

Figure 11 is a graph showing the luminance/voltage characteristics of a thin film of polymer (23).

Figure 12 is a graph showing the UV-VIS spectrum of a solution of polymer (29) in dichloromethane.

Figure 13 is a graph showing the UV-VIS spectrum of a solution of polymer (31) in dichloromethane.

Figure 14 is a graph showing the efficiency / current relationship in a thin film of a blend of compound (8) in polystyrene (50:50).

Figure 15 is a graph showing the efficiency current relationship in a thin film of a blend of polymer (41) and polystyrene (1:9).

Figure 16 is a graph showing the efficiency current relationship in a thin film of a blend of polymer (41) and polystyrene (1:4) in a bilayer device- ITO / PPV / polymer blend / Ca.

Figure 17 is a graph showing the efficiency current relationship for a thin film of a blend of polymer (42) and oxadiazole (43) (50:50)

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Example 1

Preparation of 2-hydroxy-5-tert-butylbenzaldehyde (6)

To an ice-cold stirred mixture of o-anisaldehyde (50 ml, 326 mmol) and tert-butylchloride (80 ml, 735 mmol) was added aluminium chloride (40 g, 300 mmol). The reaction mixture became thick. Dry dichloromethane (100 ml) and aluminium chloride (60 g, 450 mmol) were added carefully with cooling. Once the reaction became less vigorous the reaction mixture was stirred at room temperature for 2.25 h. Ice (50 g) and subsequently ice-cold water (100 ml) were added carefully and the mixture was left to stir for 20 min. Water (250 ml) and ether (550 ml) were added. The aqueous layer was removed and the organic layer was washed with water (3 x 250 ml), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was purified by distillation under reduced pressure and the fraction (b.p. 80-86 °C, 0.55-0.65 mm Hg) collected to yield (6) as a colourless oil (23.4 g, 40 %).

Preparation of 2-methoxy-5-tert-butylbenzaldehyde (5)

To a solution of (6) (5.01 g, 28.1 mmol) in dry DMF (25 ml) was added a solution of tetra-n-butylammonium hydroxide in methanol (1.0 M, 28.5 ml, 28.5 mmol). Methyl iodide (25 ml, 399 mmol) was added and the solution was stirred at reflux for 1.5 h and then allowed to cool. Ether (250 ml) and water (250 ml) were added. The aqueous layer was removed and the organic layer was washed with water (3 x 250 ml), brine (250 ml), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography

over silica (dichloromethane/petroleum ether [60/80]; 4:1) to yield a colourless oil of (5) (4.36 g, 81 %); δ_H (CDCl₃) 1.29 (9 H, s, tert-butyl), 3.88 (3 H, s, OCH₃), 6.95 (1 H, d, J = 8.8 Hz, H3), 7.56 (1 H, dd, J = 8.8, 2.7 Hz, H4), 7.83 (1 H, d, J = 2.7 Hz, H6), and 10.44 (1 H, s, CHO).

Preparation of 2-methoxy-5-tert-butylstilbene (4)

A suspension of dimethyl benzylphosphonate (7) and sodium hydride (60 % in oil, 0.38 g, 9.5 mmol) in dry DMF (39 ml) was cooled with stirring to 6 °C. A solution of (5) (1.45 g, 7.54 mmol) in dry DMF (14 ml) was added dropwise keeping the reaction temperature at 5-7 °C and then the reaction mixture was stirred at room temperature for 3 h under argon. Water (250 ml) and ether (400 ml) were added. The organic layer was separated and washed with water (3 x 100 ml), brine (50 ml), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane/hexane; 1:1) to yield a colourless gum of (2) (1.42 g, 71 %). (Found: C, 85.78; H, 8.36. C₁₉H₂₂O requires C, 85.67; H, 8.33 %); λ_{max}/nm (CH₂Cl₂) 291 (log ε 4.26) and 323 (4.25); δ_H (CDCl₃) 1.36 (9 H, s, tert-butyl), 3.88 (3 H, s, OCH₃), 6.85 (1 H, d, $J_{H4,H3}$ = 8.6 Hz, H3), 7.13 (1 H, d, J = 16.5 Hz, vinylic H), 7.25 (1 H, m, H4'), 7.28 (1 H, dd, $J_{H3,H4}$ = 8.6 Hz, $J_{H6,H4}$ = 2.3 Hz, H4), 7.36 (2 H, m, H3' and H5'), 7.50 (1 H, d, J = 16.5 Hz, vinylic H), 7.56 (2 H, m, H2' and H6'), and 7.61 (1 H, d, $J_{H4,H6}$ = 2.3 Hz, H6); δ_C (CDCl₃) 31.5 (CH₃), 34.1 [C(CH₃)₃], 55.6 (OCH₃), 110.5, 123.5, 124.1, 125.5, 125.6, 126.5, 127.2, 128.5, 128.8, 138.0, 143.2, and 154.85; m/z 266.167.

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Preparation of EL device

A solution of PMMA (0.035 g) and 2-methoxy-5-tert-butylstilbene (4) (0.04 g) in chloroform (5 ml) was prepared. Spin-coating at 2000 r.p.m. gave films with typical thickness of 100 nm. Violet electroluminescence was observed using an ITO/doped PMMA/Calcium device.

Example 2

Preparation of 2-methoxy-5-tert-butylbenzylalcohol (9)

A mixture of 2-methoxy-5-tert-butylbenzaldehyde (5) (2.54 g, 13.2 mmol) and lithium aluminium hydride (0.28 g, 7.4 mmol) in ether (50 ml) was stirred at reflux under nitrogen for 4 h and then allowed to cool. Water (30 ml), hydrochloric acid (3 M, 50 ml) and ether (50 ml) were added. The organic layer was separated and washed with water (2 x 50 ml), brine (50 ml), dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane) to yield a colourless oil of (9) (2.11 g, 82 %); δ_H (CDCl$_3$) 1.34 (9 H, s, tert-butyl), 3.84 (3 H, s, OCH$_3$), 4.71 (2 H, s, CH$_2$), 6.84 (1 H, d, J = 8.5 Hz, H3), 7.31 (1 H, dd, J = 8.5, 2.5 Hz, H4), and 7.36 (1 H, d, J = 2.5 Hz, H6).

Preparation of 2-methoxy-5-tert-butylbenzylchloride (10)

A solution of 2-methoxy-5-tert-butylbenzylalcohol (9) (1.91 g, 9.83 mmol) in 1,4-dioxane (20 ml) was added to hydrochloric acid (10 M, 43 ml). The reaction mixture was stirred for 10 min at room temperature. Ether (250 ml) and water (150 ml) were added. The organic layer was separated and washed with water (4 x 50 ml), dried over anhydrous sodium sulfate,

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filtered and concentrated in vacuo. The residue was purified
by column chromatography over silica (dichloromethane/hexane;
1:1) to yield (10) (1.85 g, 89 %). The ^1H NMR spectrum was
consistent with that reported by M. Tashiro, T. Yamato, and G.
Fukata, J. Org. Chem., 1978, 43, 1413.

Preparation of dimethyl 2-methoxy-5-tert-
butylbenzylphosphonate (11)

A solution of 2-methoxy-5-tert-butylbenzylchloride (10) (1.65
g, 7.76 mmol) in trimethyl phosphite (25 ml) was heated at
reflux for 22 h under argon. The excess trimethyl phosphite
was distilled off under reduced pressure and the residue was
purified by column chromatography over silica
(dichloromethane/methanol; 49:1), by distillation under
reduced pressure (b.p. 215 °C at 0.075 mm Hg) and finally by
column chromatography over silica (dichloromethane/methanol;
19:1) to yield a colourless oil of (11) (1.21 g, 55 %); δ_H
(CDCl$_3$) 1.33 (9 H, s, tert-butyl), 3.17 (2 H, d, J = 21.8 Hz,
CH$_2$P), 3.64 (3 H, s, OCH$_3$), 3.69 (3 H, s, OCH$_3$), 3.86 (3 H, s,
Ar-OCH$_3$), 6.83 (1 H, d, J = 8.6 Hz, H3), 7.08 (1 H, d, J =
16.4 Hz, vinylic H), 7.24, 7.29, 7.41, 7.48, and 7.50 (5 H, m,
PhH and vinylic H), and 7.57 (1 H, d, J = 2.4 Hz, PhH).

Preparation of 2-methoxy-5-tert-butyldistyrylbenzene (8)

A suspension of dimethyl 2-methoxy-5-tert-
butylbenzylphosphonate (11) (1.01 g, 3.53 mmol) and sodium
hydride (60 % in oil, 0.17 g, 4.25 mmol) in dry DMF (29 ml)
was cooled with stirring to 6 °C under argon. A solution of 4-
stilbenecarbaldehyde (12) (0.88 g, 4.23 mmol) in dry DMF (21
ml) was added dropwise with stirring keeping the reaction
temperature at 5 °C and then the reaction mixture was stirred
at room temperature for 3.75 h under argon. Water (100 ml) and
ether (300 ml) were added. The organic layer was separated,

washed with water (3 x 100 ml), dried over anhydrous sodium
sulfate, filtered and concentrated _in vacuo_. The residue was
purified by column chromatography over silica
(dichloromethane/hexane; 1:1) and recrystallised from
dichloromethane/hexane/methanol to yield a pale yellow solid
of (8) (0.95 g, 73 %), m.p. 129-129.5 °C; (Found: C, 88.06; H,
7.62. $C_{27}H_{28}O$ requires C, 88.00; H, 7.66 %); λ_{max}/nm (CH_2Cl_2)
362 (log ε 4.72); δ_H (CDCl$_3$) 1.36 (9 H, s, _tert_-butyl), 3.88 (3
H, s, OCH$_3$), 6.85 (1 H, d, $J_{H4,H3}$ = 8.6 Hz, H3), 7.13 (1 H, d,
J = 16.5 Hz, vinylic H), 7.125 (1 H, s, vinylic H), 7.26 (1
H, m, H4"), 7.28 (1 H, dd, $J_{H3,H4}$ = 8.6 Hz, $J_{H6,H4}$ = 2.44 Hz,
H4), 7.37 (2 H, m, H3" and H5"), 7.53 (7 H, m, H2", H6", H2',
H3', H5', H6', and vinylic H), 7.56 (2 H, m, H2' and H6') and
7.62 (1 H, d, $J_{H4,H6}$ = 2.4 Hz, H6); δ_C (CDCl$_3$) 31.5 (CH$_3$), 34.1
[C(CH$_3$)$_3$], 55.6 (OCH$_3$), 110.5, 123.5, 124.0, 125.6, 126.5,
126.7, 126.8, 127.5, 128.2, 128.4, 128.7, 136.3, 137.4, 137.5,
143.3 and 154.8; m/z 368.214.

Preparation of EL devices

A solution of PMMA (0.036 g) and 2-methoxy-5-_tert_-
butyldistyrylbenzene (8) (0.036 g) in chloroform (5 ml) was
prepared. Spin-coating at 2000 r.p.m. gave films with typical
thickness of 250 nm. Rapidly decaying blue light emission was
observed in an ITO/doped PMMA/Calcium device. The quantum
efficiency for the test device was ca. 0.2 %.

A solution of polystyrene (20 mg) and compound (8) (20 mg)
in chloroform (2 ml) was prepared. Spin-coating at 2000
r.p.m. gave films with typical thickness of 230 nm. Stable
blue emission was observed in an ITO / polymer blend / Ca
device. The internal quantum efficiency was ca. 1% with a
driving voltage of 20 V.

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Example 3

Preparation of 4-(6-hydroxyhexyloxy)benzaldehyde (13)

A solution of potassium hydroxide (13.2 g) and 4-
hydroxybenzaldehyde (20.6 g, 169 mmol) in ethanol (320 ml) was
refluxed for 30 min. 6-Bromohexanol (24.5 g, 135 mmol)
dissolved in ethanol (30 ml) were added and the reaction
mixture was refluxed for 16 h. The solvent was then removed in
vacuo. Dichloromethane (400 ml) was added to the residue. The
organic layer was washed with aqueous sodium hydroxide (1 M,
300 ml), water (500 ml) and brine (250 ml), filtered, dried
over anhydrous sodium sulfate and concentrated in vacuo.
Recrystallisation of the residue from
dichloromethane/petroleum ether yielded (13) as a pale yellow
solid (16.7 g, 45 %). The analytical data was in accordance
with that reported by C. Noel, C. Friedrich, V. Leonard, P.
LeBarney, G. Ravaux, and J.C. Dubois, Makromol. Chem.,
Macromol. Symp., 1989, 24, 283.

Preparation of 6-(2',5'-dimethoxy-4-stilbenoxy)hexanol (14)

A mixture of dimethyl 2,5-dimethoxybenzylphosphonate (2.92 g,
11.2 mmol) and sodium hydride (60 % in oil, 1.08 g, 27.0 mmol)
in dry DMF (92 ml) was cooled with in an ice-bath under argon.
To this was added dropwise a solution of 4-(6-
hydroxyhexyloxy)benzaldehyde (13) (2.50 g, 11.3 mmol) in dry
DMF (55 ml). The reaction mixture was stirred at 6 °C for 1.5
h and then at room temperature for 4 h. Ether (300 ml) and

water (250 ml) were added and the mixture shaken well. The organic layer was separated and washed with water (4 x 250 ml), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane/methanol; 19:1) to yield (14) (1.89 g, 47 %) as an oil; δ_H (CDCl$_3$) 1.46 (4 H, m, CH$_2$), 1.60 (2 H, m, CH$_2$), 1.79 (2 H, m, CH$_2$), 3.65 (2 H, t, J = 6.6 Hz, OCH$_2$), 3.81 (3 H, s, OCH$_3$), 3.83 (3 H, s OCH$_3$), 3.96 (2 H, t, J = 6.5 Hz, OCH$_2$), 6.76 (1 H, dd, $J_{H3',H4'}$ = 8.9 Hz, $J_{H6',H4'}$ = 3.0 Hz, H4'), 6.82 (1 H, d, $J_{H4',H3'}$ = 8.9 Hz, H3'), 6.87 and 7.45 (4 H, AA'BB', PhH), 7.03 (1 H, d, J = 16.5 Hz, vinylic H), 7.13 (1 H, d, $J_{H4',H6'}$ = 3.0 Hz, H6') and 7.31 (1 H, d, J = 16.5 Hz, vinylic H); δ_C (CDCl$_3$) 25.5, 25.6, 29.2, 32.6, 55.7, 56.2, 62.8, 67.8, 111.3, 112.2, 113.1, 114.5, 120.7, 127.6, 127.7, 128.7, 130.4, 151.2, 153.7 and 158.7.

Preparation of 6-(2',5'-dimethoxy-4-stilbenoxy)hexyl methacrylate (15)

Methacryloyl chloride (90 %, 0.52 ml, 4.8 mmol) was added dropwise to a stirred solution of 6-(2',5'-dimethoxy-4-stilbenoxy)hexanol (14) (1.54 g, 4.32 mmol) and dry triethylamine (0.76 ml, 5.5 mmol) in dry tetrahydrofuran (25 ml) under argon. The reaction mixture was stirred at 60 °C for 23 h. Ether (200 ml) and water (100 ml) were added. The organic layer was washed with water (3 x 100 ml), dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane/hexane; 4:1 to 1:0) to yield (15) (1.48 g, 81

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%) as an oil; δ_H (CDCl$_3$) 1.48 (4 H, m, CH$_2$), 1.70 (2 H, m, CH$_2$), 1.80 (2 H, m, CH$_2$), 1.95 (3 H, m, CH$_3$), 3.81 (3 H, s, OCH$_3$), 3.83 (3 H, s, OCH$_3$), 3.96 (2 H, t, J = 6.4 Hz, CCH$_2$), 4.16 (2 H, t, J = 6.6 Hz, OCH$_2$), 5.55 (1 H, m, H$_A$), 6.10 (1 H, m, H$_B$), 6.76 (1 H, dd, $J_{H3',H4'}$ = 8.2 Hz, $J_{H6',H4'}$ = 2.9 Hz, H4'), 6.82 (1 H, d, $J_{H4',H3'}$ = 8.2 Hz, H3'), 6.87 and 7.46 (4 H, AA'BB', H2, H3, H5, and H6), 7.04 (1 H, d, J = 16.5 Hz, vinylic H), 7.13 (1 H, d, $J_{H4',H6'}$ = 2.9 Hz, H6') and 7.32 (1 H, d, J = 16.4 Hz, vinylic H); δ_C (CDCl$_3$) 18.3, 25.69, 25.74, 28.5, 29.1, 53.4, 55.7, 56.2, 64.6, 67.7, 111.3, 112.2, 113.1, 114.5, 120.9, 125.2, 127.5, 127.7, 128.8, 130.4, 136.4, 151.2, 153.7, 158.6 and 167.4.

Polymerisation of 6-(2',5'-dimethoxy-4-stilbenoxy)hexyl methacrylate (15)

To a solution of 6-(2',5'-dimethoxy-4-stilbenoxy)hexyl methacrylate (15) (1.08 g, 2.54 mmol) in dry toluene (5 ml) was added azobis(isobutyronitrile) (1.16 g, 8.78 mmol) over 10 min in several aliquots. The reaction mixture was then stirred at 88 °C for 1 h under argon. The solvent was completely removed. The oily residue was reprecipitated twice from a dichloromethane/hexane mixture. It was then dissolved in dichloromethane, filtered through sodium sulfate and concentrated _in vacuo_ to furnish pure polymer (16) (286 mg, 27 %).

Example 4

Preparation of 2'-methoxy-5'-_tert_-butylstilbene-4-carbaldehyde (17)

Dimethyl 2-methoxy-5-_tert_-butylbenzylphosphonate (11) (16.3 g, 57.0 mmol) and sodium hydride (60 % in oil, 4.56 g, 114 mmol) in dry DMF (100 ml) were stirred under argon in an ice bath. A solution of terephthaldehyde mono(diethyl acetal) (17.8 ml, 85.4 mmol) in dry DMF (60 ml) was then added dropwise. The mixture was left to stir overnight. The pale yellow reaction

mixture was combined with water (75 ml) and hydrochloric acid
(3 M, 45 ml) and stirred for 10 min. Then water (500 ml) and
ether (600 ml) were added. The organic layer was washed with
water (4 x 750 ml), brine (500 ml), dried over anhydrous
sodium sulfate, filtered and concentrated in vacuo. The
residue was purified by column chromatography over silica
(dichloromethane/hexane; 4:1) and by recrystallisation from
hot petroleum ether (30-40) to yield (17) (11.6 g, 69 %) as a
pale yellow solid, m.p. 82-83 °C; (Found: C, 81.75; H, 7.39.
$C_{20}H_{22}O_2$ requires C, 81.60; H, 7.53 %); δ_H (CDCl$_3$) 1.37 (9 H,
s, tert-butyl), 3.88 (3 H, s, OCH$_3$), 6.86 (1 H, d, J = 8.7 Hz,
PhH), 7.18 (1 H, d, J = 16.4 Hz, vinylic H), 7.32 (1 H, dd, J
= 8.5, 2.4 Hz, PhH), 7.62 (1 H, d, J = 2.6 Hz, PhH), 7.65 (1
H, d, J = 16.8 Hz, vinylic H), 7.68 and 7.85 (4 H, AA'BB',
PhH) and 9.98 (1 H, s, CHO).

Preparation of 2'-methoxy-5'-tert-butylstilbene-4-methanol
(18)

A solution of 2'-methoxy-5'-tert-butylstilbene-4-carbaldehyde
(17) (11.4 g, 38.6 mmol) in dry tetrahydrofuran (30 ml) was
added dropwise to a mixture of lithium aluminium hydride (0.82
g, 22 mmol) in dry ether (100 ml). The reaction mixture was
refluxed overnight. Then water (60 ml), hydrochloric acid (3
M, 100 ml) and ether (250 ml) were added. The organic layer
was washed with water (2 x 250 ml), brine (150 ml), dried over
anhydrous sodium sulfate, filtered and concentrated in vacuo.
The residue was purified by column chromatography over silica
(dichloromethane) and by recrystallisation from hot hexane to
yield (18) (4.94 g, 43%) in form of colourless crystals, m.p.
103-104 °C; (Found: C, 81.14; H, 8.16. $C_{20}H_{24}O_2$ requires C,
81.04; H, 8.16 %); m/z 296 (96, M$^+$), 281 (100), 263 (34 %).

Preparation of 5'-tert-butyl-4-chloromethyl-2'-methoxy-
stilbene (19)

A solution of 2'-methoxy-5'-tert-butylstilbene-4-methanol (18)
(5.83 g, 19.7 mmol) in 1,4-dioxane (25 ml) was poured into

concd. hydrochloric acid (120 ml). A colourless precipitate appeared immediately. The mixture was stirred for 1 h. Then dichloromethane (250 ml) was added. The organic layer was washed with water (500 ml), brine (250 ml), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane) and by recrystallisation from hot hexane to yield (19) (4.26 g, 69 %) in form of colourless crystals, m.p. 103-104 °C; (Found: C, 76.42; H, 7.42. $C_{20}H_{24}ClO$ requires C, 76.30; H, 7.36 %); δ_H (CDCl$_3$) 1.40 (9 H, s., tert-butyl), 3.90 (3 H, s, OCH$_3$), 4.62 (2 H, s, CH$_2$Cl), 6.88 (1 H, d, J = 8.7 Hz, PhH), 7.17 (1 H, d, J = 16.5 Hz, vinylic H), 7.32 (1 H, dd, J = 8.6, 2.5 Hz, PhH), 7.40 and 7.57 (4 H, AA'BB', PhH), 7.54 (1 H, d, J = 16.0 Hz, vinylic H), 7.65 (1 H, d, J = 2.4 Hz., PhH); m/z 316, 314 (35, 100, M$^+$), 301, 299 (29, 91 %).

Preparation of phosphonate (20)

A solution of 5'-tert-butyl-4-chloromethyl-2'-methoxy-stilbene (19) (4.16 g, 13.2 mmol) in trimethyl phosphite (48 ml) was refluxed for 24 h. The solvent was then distilled off in vacuo. The residue was purified by column chromatography over silica (dichloromethane) to yield (20) (3.61 g, 70 %) as a pale yellow oil; δ_H (CDCl$_3$) 1.33 (9 H, s, tert-butyl), 3.17 (2 H, d, J = 21.8 Hz, CH$_2$P), 3.64 (3 H, s, OCH$_3$), 3.69 (3 H, s, OCH$_3$), 3.86 (3 H, s, aromatic OCH$_3$), 6.83 (1 H, d, J = 8.6 Hz, PhH), 7.07 (1 H, d, J = 16.4 Hz, vinylic H), 7.24-7.57 (5 H, m, vinylic and PhH).

Preparation of distyrylbenzene (21)

A solution of phosphonate (20) (3.43 g, 8.77 mmol) in dry DMF
(100 ml) was added to sodium hydride (60 % in oil, 0.96 g, 24
mmol). The solution was cooled in an ice bath and a solution
of 4-(6-hydroxyhexyloxy)benzaldehyde (13) (2.08 g, 9.36 mmol)
in dry DMF (50 ml) was added dropwise over 30 min. The
reaction mixture was stirred at 6 °C for 1.5 h and then at
room temperature for 4 h. Water (250 ml) was added and the
mixture extracted with ether (2 x 200 ml). The organic layer
was separated and washed with water (3 x 300 ml), dried over
anhydrous magnesium sulfate, filtered and concentrated _in_
vacuo. The residue was purified by column chromatography over
silica (dichloromethane/methanol; 10:1) and recrystallised
from dichloromethane/hexane to yield (21) (3.08 g, 72 %), m.p.
118-120 °C; (Found: C, 81.77; H, 8.31. $C_{33}H_{40}O_3$ requires C,
81.94; H, 8.43 %); δ_H (CDCl$_3$) 1.36 (9 H, s, _tert_-butyl), 1.40-
1.86 [8 H, m, (CH$_2$)$_4$], 3.66 (2 H, t, J = 6.5 Hz, OCH$_2$), 3.88
(3 H, s, OCH$_3$), 3.96 (2 H, t, J = 6.4 Hz, OCH$_2$), 6.84-7.65 (15
H, m, phenyl and vinylic H); m/z 484 (66, M$^+$), 202 (42), 143
(70), 105 (100 %).

Esterification of (21) with methacryloyl chloride

To a stirred solution of alcohol (21) (3.05 g, 6.29 mmol) and
dry triethylamine (1.25 ml) in dry tetrahydrofuran (25 ml)
under argon was added dropwise methacryloyl chloride (90 %,
0.68 ml, 7.0 mmol). The reaction mixture was stirred at 55 °C
for 2 h. The solution was poured into ether (200 ml). The
organic layer was separated and washed with water (3 x 200
ml), dried over anhydrous magnesium sulfate, filtered and
concentrated _in vacuo_. The oily residue was purified by column
chromatography over silica (dichloromethane/hexane; 1:1) to

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yield (22) (3.93 g, 84 %) as a viscous yellow oil, m.p. 83-84.5 °C; (Found: C, 80.09; H, 7.96. $C_{37}H_{44}O_4$ requires C, 80.40; H, 8.00 %); δ_H (CDCl$_3$) 1.37 (9 H, s, tert-butyl), 1.40-1.32 [8 H, m, (CH$_2$)$_4$], 1.97 (3 H, s, CH$_3$), 3.88 (3 H, s, OCH$_3$), 3.98 (2 H, t, J = 6.2 Hz, OCH$_2$), 4.18 (2 H, t, J = 6.5 Hz, OCH$_2$), 5.56 and 6.12 (2 H, s, =CH$_2$), 6.83-7.63 (15 H, m, PhH and vinylic H); m/z 552.324.

Polymerisation of (22)

To a deoxygenated solution of methacrylate (22) (2.60 g, 4.70 mmol) in dry toluene (30 ml) was added dropwise over 5 h a solution of azobis(isobutyronitrile) (50 mg) in toluene (5 ml) at 90 °C. The reaction mixture was then allowed to cool and ether (20 ml) was added. The oily precipitate was reprecipitated twice from dichloromethane/ether to furnish the least soluble fraction of polymer (23) (210 mg, 8 %). To the supernatant liquid was added excess ether (120 ml) to obtain another fraction of polymer (23) (1.22 g, 47 %), m.p. 124-132 °C; (Found: C, 79.67; H, 8.16; N, 0.27. $C_{37}H_{44}O_4$ requires C, 80.40; H, 8.00; N, 0.00 %); λ_{max}/nm (CHCl$_3$) 360 (onset of absorption at 415 nm); ν_{max}/cm^{-1} 2946m, 2861m, 1724s, 1604m, 1513s, 1494m, 1173s, 1149m, 962m; δ_H (CDCl$_3$) 0.90-2.10 (br. m, aliphatic CH), 1.38 (br. s, tert-butyl), 3.67 (br. s, OCH$_3$), 3.95 (br. s, OCH$_2$), 6.79-7.67 (m, phenyl and vinylic H).

Preparation of EL device

A solution of poly(methacrylate) (23) (0.2 g) in chloroform (5 ml) was prepared. Spin-coating at 2000 r.p.m. gave films with typical thickness of 300 nm. Blue(violet) electroluminescence was observed in an ITO/doped PMMA/Calcium device. The internal quantum efficiency was 0.015% at a drive voltage of 44 V.

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Example 5
Preparation of 4-(tert-
butyldimethylsilyloxymethyl)benzylalcohol (24)

A mixture of 1,4-benzenedimethanol (5.10 g, 36.9 mmol) and
sodium hydride (60 % in oil, 1.21 g) in dry tetrahydrofuran
(75 ml) was stirred at room temperature for 80 min. tert-
Butyldimethylchlorosilane (6.34 g) was added and the reaction
mixture was stirred for further 60 min. Ether (250 ml) was
added. The organic layer was then washed with saturated sodium
bicarbonate (100 ml), brine (150 ml), dried over anhydrous
sodium sulfate, filtered and concentrated in vacuo. The
residue was purified by column chromatography over silica
(ethyl acetate/hexane; 1:4) to yield 4-(tert-
butyldimethylsilyloxymethyl)benzylalcohol (24) (4.47 g, 48 %);
v_{max}/cm^{-1} 3620m, 3480w, 2920s, 2850s, 1460m, 1370s, 1080s; δ_H
(CDCl$_3$) 0.11 (6 H, s, SiCH$_3$), 0.95 (9 H, s, tert-butyl), 2.35
(1 H, bs, OH), 4.61 (2 H, s, CH$_2$O), 4.74 (2 H, s, CH$_2$O) and
7.30 (4 H, s, PhH); δ_C (CDCl$_3$) -5.2, 18.4, 26.0, 64.8, 65.0,
126.3, 127.0, 139.6 and 140.8.

Preparation of 4-(tert-
butyldimethylsilyloxymethyl)benzaldehyde (25)

A solution of oxalylchloride (1.6 ml) in dry dichloromethane
(37 ml) was cooled to -70 °C under N$_2$. Dry dimethylsulfoxide
(2.5 ml) in dichloromethane (10 ml) and a solution of 4-(tert-
butyldimethylsilyloxymethyl)benzylalcohol (24) (3.94 g, 15.6
mmol) in dichloromethane (20 ml) were added carefully. The
reaction mixture was stirred at -70 °C for 1 h. Dry
triethylamine (12 ml) was then added. The reaction mixture was
allowed to warm up to 0 °C. Saturated aqueous sodium
bicarbonate (50 ml) was added, the organic layer was separated
and the aqueous layer was extracted with dichloromethane (4 x
50 ml). The combined organic extracts were dried over

anhydrous sodium sulfate, filtered and concentrated in vacuo.
The residue was purified by column chromatography over silica
(dichloromethane/hexane; 4:1) to yield 4-(tert-
butyldimethylsilyloxymethyl)benzaldehyde (25) (3.21 g, 82 %);
v_{max}/cm^{-1} 2920s, 2850s, 2730w, 1700s, 1090s; δ_H (CDCl$_3$) 0.11 (6
H, s, SiCH$_3$), 0.94 (9 H, s, tert-butyl), 4.80 (2 H, s, CH$_2$O),
7.47 and 7.84 (4 H, AA'BB', PhH) and 9.98 (1 H, s, CHO); δ_C
(CDCl$_3$) -5.3, 18.4, 25.9, 64.4, 126.2, 129.8, 135.3, 148.6 and
192.0; m/z 251.1467 (M$^+$ + H).

Preparation of disilylated diol (27)

To a solution of 2,5-dimethoxy-p-xylylene-α,α'-
bis(triphenylphosphonium chloride) (26) (3.48 g, 4.58 mmol),
obtained from 1,4-bis(chloromethyl)-2,5-dimethoxybenzene and
triphenylphosphine, and 4-(tert-
butyldimethylsilyloxymethyl)benzaldehyde (25) (2.53 g, 10.1
mmol) in dry ethanol (45 ml) was added a freshly prepared
solution of sodium ethoxide in ethanol (13 ml). The reaction
mixture was stirred under N$_2$ for 65 min. The solvent was then
completely removed and the residue was purified by column
chromatography over silica (dichloromethane/hexane; 1:1) to
give disilyl-protected diol (27) (915 mg, 32 %); δ_H (CD$_2$Cl$_2$)
0.13 (6 H, s, SiCH$_3$), 0.96 (9 H, s, tert-butyl), 3.93 (6 H, s,
OCH$_3$), 4.75 (2 H, s, CH$_2$O), 7.16 (2 H, d, J = 16.5 Hz, vinylic
H), 7.17 (2 H, s, ArH), 7.33 and 7.53 (4 H, AA'BB', ArH), 7.48
(2 H, d, J = 16.5 Hz, vinylic H); δ_C (CD$_2$Cl$_2$) -5.3, 18.5,
25.9, 56.4, 65.0, 109.1, 122.8, 126.57, 126.64, 126.8, 128.8,
136.8, 141.3, 151.7; m/z 630.3561 (M$^+$).

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Preparation of diol (28)

A solution of the diprotected material (27) (79.3 mg, 0.126
mmol) in dichloromethane (3 ml) and tetra-n-butylammonium
fluoride (1.0 M in tetrahydrofuran, 1.0 ml) was stirred under
N_2 at 0 °C for 1 h. Saturated aqueous sodium bicarbonate (5
ml) was added. The organic layer was separated and the aqueous
layer was extracted with dichloromethane (4 x 10 ml). The
combined organic layers were dried over anhydrous sodium
sulfate, filtered and concentrated in vacuo. The residue was
purified by column chromatography over silica
(dichloromethane) to give diol (28) (52.1 mg, 66 %); λ_{max}/nm
(CH_2Cl_2) 392 (log ϵ 4.617) and 327 (4.421); v_{max}/cm^{-1} 3320bm,
1209s, 1043s, 966s; δ_H ($CDCl_3$) 3.93 (6 H, s, OCH_3), 4.68 (4 H,
s, CH_2OH), 7.16 (2 H, d, J = 16.5 Hz, vinylic H), 7.17 (2 H,
s, ArH), 7.36 and 7.56 (4 H, AA'BB', ArH), 7.49 (2 H, d, J =
16.5 Hz, vinylic H); δ_C (CD_2Cl_2) 56.4, 65.1, 109.1, 123.2,
126.6, 126.8, 127.5, 128.7, 137.3, 140.8, 151.7; m/z 402.1831.

Preparation of Polymer (29)

To a solution of sebacoyl chloride (0.120 g, 0.5 mmol) in dry
tetrahydrofuran (2 ml) under argon was added a solution of
diol (28) (0.202 g, 0.5 mmol) and pyridine (0.12 ml, 1.3 mmol)
in dry tetrahydrofuran (5 ml). After stirring for 2 h, during
which time a white solid precipitated, dichloromethane (20 ml)
was added. The solution was washed with hydrochloric acid (1
M, 20 ml) and water (3 x 20 ml) and the solvent evaporated in

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<u>vacuo</u> to a volume of ca. 5 ml. Hexane (20 ml) was added and a
yellow precipitate was filtered off and washed with hexane.
The solid was redissolved in dichloromethane (5 ml),
reprecipitated with ethanol (25 ml), filtered and washed with
ethanol to yield (29) (0.20 g, 71 %) as a yellow solid, m.p.
97-112 °C. The ^{1}H NMR and microanalytical analyses indicate an
oligomer of formula (diol)$_6$(diacid)$_7$; λ_{max}/nm (CH$_2$Cl$_2$) 392
(onset of absorption at 445 nm) and 327 (cf. Figure 12);
ν_{max}/cm^{-1} 3035w, 1734s, 1608m, 1210s, 1164s, 1042s, 966s. δ_H
(CDCl$_3$) 1.01 (s, alkyl), 1.45 (bs, alkyl), 2.16 (t, $\hat{J}$ = 7.6
Hz, CH$_2$CO$_2$), 3.72 (s, OMe), 4.91 (s, CH$_2$O), 6.9-7.4 (m, phenyl
and vinylic H); [Found: C, 75.28; H, 7.12%. Oligomer
(diol)$_6$(diacid)$_7$ requires C, 75.09; H, 7.09%].

Preparation of EL Device

A solution of the polymer (29) (30 mg) in chloroform (1ml)
was prepared. Spin-coating at 2000 r.p.m. gave films with
thickness of 300 nm. Blue-green electroluminescence was
observed in an ITO / polymer / Ca device. The internal
quantum efficiency was 0.01 % at a drive voltage of 50 V.

Example 6

A solution of thiophenol (0.18 ml, 1.8 mmol) in methanolic
tetra-<u>n</u>-butylammonium hydroxide (1.0 M, 1.8 ml, 1.8 mmol) was
added to a solution of sulfonium precursor polymer (30) (4 %
w/w, 5.0 g) in methanol. A creamy white precipitate formed
almost immediately. The polymer was collected by suction
filtration and dissolved in chloroform (50 ml). The clear,
pale green solution was poured onto methanol (800 ml). The
precipitate was again collected by suction filtration and
dried to yield polymer (31) in form of a pale green solid (126
mg); λ_{max}/nm (CH$_2$Cl$_2$) cf. Figure 13.

Example 7

4-Mercaptomethylstilbene (32a)

A mixture of 4-chloromethylstilbene (2.27 g, 10.8 mmol) and
thiourea (0.93 g, 12 mmol) in ethanol (70 ml) was heated to
reflux for 20 h. Aqueous sodium hydroxide (2.5 M, 11 ml) was
added to the hot solution and the reaction mixture was stirred
for further 6 h. Sulfuric acid (10 %, 40 ml) was then added
and the mixture left overnight. Water (400 ml), ether (450 ml)
and dichloromethane (200 ml) were added. The organic layer was
separated and concentrated in vacuo and the residue purified
by column chromatography over silica (dichloromethane/hexane;
4:1) to give (32a) (1.69 g, 83 %), m.p. 105-107 °C; (Found:
C, 79.70; H, 6.01; S, 14.32. $C_{15}H_{14}S$ requires C, 79.60; H,
6.24; S, 14.16 %); λ_{max}/nm (CH_2Cl_2) 302 (log ε 4.49) and 315
(4.50); δ_H ($CDCl_3$) 1.78 (1 H, t, J = 7.5 Hz, SH), 3.76 (2 H,
d, J = 7.5 Hz, CH_2S), 7.10 (2 H, s, PhH or vinylic H), 7.33
and 7.50 (9 H, m, PhH or vinylic H).

Attachment of (32a) to dimethoxy-PPV precursor polymer (34)

A mixture of bis-sulfonium salt (33) (1.03 g, 2.50 mmol) and
methanol (6.4 ml) was deoxygenated and cooled with an ice-
bath. A methanolic tetra-n-butylammonium hydroxide solution
(0.4 M, 6.2 ml) was added dropwise. The precipitate slowly
dissolved and a greenish viscous solution formed. The reaction
mixture was stirred for 1 h at 0 °C and was neutralised by
addition of a solution of hydrogen chloride in methanol. 4-
Mercaptomethylstilbene (32a) (678 mg), dichloromethane (3 ml)
and a methanolic tetra-n-butylammonium hydroxide solution (0.4
M, 8.0 ml) were added. The reaction mixture became greenish
yellow and a yellow precipitate formed slowly. Dichloromethane
(15 ml) was added to dissolve the residue. The reaction

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mixture was further stirred for 16 h at room temperature. It was then concentrated and diluted with methanol (50 ml). The precipitate was collected by suction filtration and washed with methanol (50 ml) and ether (50 ml). The residue (35a) was dissolved in chloroform.

Example 8

2,5-Dimethoxystilbene-4'-methanol

Sodium hydride (60 % in oil, 2.93 g) and dimethyl 2,5-dimethoxybenzylphosphonate (6.73 g, 25.9 mmol) in dry DMF (80 ml) were stirred at room temperature under N_2 for 45 min. The reaction mixture was cooled in an ice bath and a solution of terephthaldehyde mono(diethyl acetal) was added dropwise over 25 min. After stirring for 3 h, water (25 ml) was added dropwise, followed by hydrochloric acid (10 M, 20 ml), ether (300 ml) and more water (400 ml). The organic layer was separated, washed with water (3 x 250 ml), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane). The crude 2,5-dimethoxystilbene-4'-carbaldehyde (4.13 g) obtained, lithium aluminium hydride (1.92 g) and ether (250 ml) were heated to reflux for 3 days. Water (50 ml), followed by hydrochloric acid (3 M, 110 ml) were then added. The organic layer was separated, washed with water (2 x 250 ml), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane/methanol; 39:1) to give some 4,4'-(2,5-dimethoxystyryl)benzene and the desired 2,5-dimethoxystilbene-4'-methanol (1.81 g, 26 %); δ_H (CDCl$_3$) 1.98 (1 H, bs, OH), 3.81 (3 H, s, OCH$_3$), 3.84 (3 H, s, OCH$_3$), 4.66 (2 H, s, CH$_2$O),

6.79 (1 H, dd, J = 7.7, 2.8 Hz), 6.83 (1 H, d, J = 7.7 Hz),
7.08 and 7.46 (2 H, d, J = 16.5 Hz, vinylic H), 7.15 (1 H, d,
J = 2.8 Hz), 7.32 and 7.52 (4 H, AA'BB'); δ_C (CDCl$_3$) 55.7,
65.0, 111.6, 112.2, 113.7, 123.2, 126.7, 127.1, 127.2, 128.9,
137.1, 140.1, 151.4, and 153.7.

4'-Chloromethyl-2,5-dimethoxystilbene

2,5-Dimethoxystilbene-4'-methanol (1.18 g, 4.36 mmol) in
dichloromethane (3 ml) and hydrochloric acid (10 M, 100 ml)
was stirred for 1 h at room temperature. Ether (100 ml) and
water (100 ml) were added and the organic layer separated,
washed with water (2 x 125 ml), dried over anhydrous sodium
sulfate, filtered and concentrated in vacuo. The residue was
purified by column chromatography over silica
(dichloromethane) to give 4'-chloromethyl-2,5-
dimethoxystilbene (856 mg, 68 %); δ_H (CDCl$_3$) 3.83 (3 H, s,
OCH$_3$), 3.85 (3 H, s, OCH$_3$), 4.59 (2 H, s, CH$_2$Cl), 6.81 (1 H,
dd, J = 8.8, 2.7 Hz), 6.85 (1 H, d, J = 8.8 Hz), 7.10 and 7.49
(2 H, d, J = 16.5 Hz, vinylic H), 7.17 (1 H, d, J = 2.7 Hz),
7.37 and 7.53 (4 H, AA'BB'); δ_C (CDCl$_3$) 46.1, 55.7, 56.0,
111.5, 112.2, 113.6, 123.9, 126.8, 128.4, 128.7, 136.4, 137.9,
151.4 and 153.6.

4'-Mercaptomethyl-2,5-dimethoxystilbene (32b)

A solution of 4'-chloromethyl-2,5-dimethoxystilbene (856 mg, 2.96 mmol), thiourea (0.29 g, 3.8 mmol), and ethanol (16 ml) was heated to reflux for 3.5 h. Aqueous sodium hydroxide (2.5 M, 2.8 ml) was added and the mixture refluxed for further 2 h. The reaction mixture was allowed to cool and dichloromethane (50 ml), ether (200 ml) and sulfuric acid (10 %, 10 ml) were added. The organic layer was separated, washed with water (2 x 200 ml), brine (100 ml), dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by column chromatography over silica (dichloromethane/hexane; 4:1) to give (32b) (328 mg, 39 %); v_{max}/cm^{-1} 2950s, 1490m, 1470s, 1430m, 1390s, 1215s, 1180s, 1050s.

Attachment of (32b) to dimethoxy-PPV precursor polymer (34)

A mixture of bis-sulfonium salt (33) (1.03 g, 2.50 mmol) and methanol (6.4 ml) was deoxygenated and cooled with an ice-bath. A methanolic tetra-n-butylammonium hydroxide solution (0.4 M, 6.2 ml) was added dropwise. The precipitate slowly dissolved and a greenish viscous solution formed. The reaction mixture was stirred for 1 h at 0 °C and was neutralised by addition of a solution of hydrogen chloride in methanol. A solution of (32b) (303 mg) in methanolic tetra-n-butylammonium hydroxide (0.4 M, 2.8 ml) was added. A precipitate formed rapidly. Dichloromethane (4 ml) was added to dissolve the residue. The reaction mixture was further stirred for 16 h at room temperature. It was then concentrated and diluted with methanol (50 ml). The precipitate was collected by suction filtration and washed with methanol (100 ml) and ether (100 ml). The residue (35b) was dissolved in chloroform to give a greenish yellow solution.

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Example 9

Attachment of (32a) to PPV precursor polymer (36)

A solution of tetrabutylammonium hydroxide (1.0 M in
methanol, 0.44 ml) and mercaptomethylstilbene (32b) (0.112
g, 0.52 mmol) in THF (15 ml) was added slowly to a solution
of the tetrahydrothiophene precursor to PPV (36) in
methanol (7.9 g of a 1.5 % w/w solution in methanol) under
argon, and stirred for 2 h. The resulting yellow
precipitate was filtered off and dried under vacuum.
Dichloromethane (40 ml) was added, followed by a solution
of tetrabutylammonium hydroxide (1.0 M in methanol, 0.24
ml) and mercaptomethylstilbene (32b) (0.064 g, 0.28 mmol)
in THF (10 ml) and the mixture was stirred for 12 h under
argon. During this time the precipitate broke up and
partially dissolved. The solution was filtered, and the
filtrate was concentrated *in vacuo* to a volume of *ca.* 10
ml. Methanol was added and the resulting precipitate was
recovered by filtration and dried to yield (37) (65 mg) as
a yellow powder. GPC analysis against polystyrene standards
in chloroform indicated a number average molecular weight
of 10,000.

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Example 10

1,4-Dibromo-2,5-dihexyloxybenzene (**38**)

A solution of bromine (110 mmol, 17.2 g) in chloroform (30 ml) was added to a solution of dihexyloxybenzene (54.0 mmol, 15.0 g) in chloroform (100 ml) at room temperature over 1 h. After a further 18h, the brown mixture was washed with aqueous sodium metabisulphite (50 ml), aqueous $NaHCO_3$ (1 M, 50 ml x 2), water (50 ml) and brine (50 ml), dried ($MgSO_4$), evaporated and dried under vacuum to give a colourless solid (23.2 g). Further purification was achieved by recrystallisation from methanol (180 ml) to give a pure product (21.7 g, 93 %); m. p. 62-63 °C; Rf (dichloromethane) 0.77; υ_{max} (KBr/cm^{-1}) 2920 (C-H), 1500 (Ph), 1220 (Ph-O), 1020 (C-O); δ_H (400 MHz, $CDCl_3$) 0.89 (6H, t, J 6.9, Me) 1.32 (8H, m), 1.47 (4H, m), 1.78 (4H, m), 3.93 (4H, t, J 6.5), 7.07 (2H, s, Ph); δ_c (100 MHz, $CDCl_3$) 14.0 (Me), 22.5, 25.6, 29.0, 31.4, 70.2, 111.1 (PhC-Br), 118.4 (PhC-H), 150.0 (PhC-O).

1-Bromo-2,5-dihexyloxybenzene-4-boronic acid (**39**)

Butyllithium (48.2 mmol, 30.2 ml, 15 % in hexane) was added into a solution of 1,4-dibromo-2,5-dihexyloxybenzene (48.2 mmol, 21.0 g) in ether (195 ml) under argon at between -10 to -30 °C over 15 min. The mixture was allowed to warm to room temperature and was stirred for further 2h. It was then transferred into a solution of freshly distilled trimethyl borate (145 mmol, 16.4 ml) in ether (390 ml) under argon at -60 °C. The mixture was allowed to warm to room temperature and was stirred for further 15h. Aqueous hydrochloric acid (2 M, 300ml) was added into the mixture, and the aqueous layer was separated and extracted with ether (100 ml x 2). The combined organic layer was evaporated and 40/60 petroleum ether (200 ml) was added. A colourless solid was recovered by filtration and dried under vacuum. Further purification was carried out by column chromatography over silica (60

g), with toluene (200 ml) as an eluent to remove by-
products. Elution with ether (300 ml) produced a pure
product. (8.9 g, 46 %); m. p. 102-103 °C; Rf (ether),
0.71; υ_{max} (KBr, cm⁻¹) 3360 (OH), 2940 (C-H), 1200 (Ph),
1040 (C-O), 810 (Ph); δ_H (400 MHz, CDCl₃) 0.91 (6H, m,
Me), 1.33 (8H, m), 1.44 (4H, m) 1.80 (4H, m) 4.00 (4H, m),
6.48 (2H, s, OH), 7.09 (1H, s, Ph), 7.36 (1H, s, Ph); δ_c
(100 MHz, CDCl₃) 13.9, 22.5, 25.5, 29.1, 31.4, 69.6,
116.3, 116.4 (PhC-H), 118 (br, C-B), 120.5 (PhC-H), 149.6
(PhC-O), 158.0 (PhC-O).

4-Bromobenzeneboronic acid (40)

A solution of butyllithium (21.2 mmol, 15 %, 13.3 ml) in
hexane was slowly added to a solution of 1,4-
dibromobenzene (21.2 mmol, 5.0 g) in ether (86 ml) at -40
°C under argon. The mixture was allowed to warm to room
temperature and was stirred for further 2h. The mixture
was transferred into a solution of freshly distilled
trimethyl borate (63.3 mmol, 7.2 ml) in ether (172 ml) at
-60 °C under argon. The mixture was allowed to warm to
room temperature and refluxed for further 20h. Aqueous
hydrochloric acid (2 M, 127 ml) was added, and the aqueous
phase was separated and extracted with ether (90 ml). The
solvent was removed from the combined organic layers and
petroleum ether was added. A colourless solid was
recovered by filtration (ca 5 g). Further purification was
carried out by column chromatography over silica (64 g),
with toluene (200 ml) as an eluent to remove by-products.
Elution with ether (300 ml) produced a pure product. (2.0 g,
48 %); m. p. 282-283 °C, Rf (ether), 0.42; υ_{max} (KBr, cm⁻
¹) 3020 (Ph), 1580 (Ph), 830 (Ph); δ_H (250 MHz, CDCl₃)
4.63 (2H, s, OH), 7.64 (2H, d, J 6.6, 3,5-PhH), 8.05 (2H,
d, J 6.6, 2,6-PhH).

Poly (2,5-di-n-hexyloxy-phenylene) (41)

A mixture of 1-bromo-2,5-dihexyloxybenzeneboronic acid (1.0
mmol, 400 mg), Pd(PPh₃)₄ (4.1 mmol, 4.8 mg), toluene (5.0

ml) and aqueous Na_2CO_3 (2 M, 3.2 ml) were refluxed for 48h
under argon. The mixture was poured into acetone (20ml). A
dark solid was recovered by filtration, washed with aqueous
HCl (2 M, 30 ml) and dried under vacuum (0.48 g). Further
purification was carried out by extraction in a Soxhlet
apparatus with chloroform (120 ml) for 19h. After the
solvent was removed, the residue was poured into acetone
(20 ml). A grey solid was recovered by filtration and
dried. Its fluorescence colour was violet. (119 mg, 43 %);
(Found: C, 77.2; H, 10.2. $C_{18}H_{30}O_2$ requires C, 77.6; H, 10.9
%); υ_{max} (KBr, cm^{-1}) 2920 (C-H), 1460 (Ph), 1210 (Ph-O),
1060 (C-O), 840 (Ph); δ_H (250 MHz, CDCl$_3$) 0.87 (6H, d, J
5.5, Me), 1.28 (12H, s), 1.68 (4H, d, J 6.1), 3.92 (4H, t,
J 5.4), 7.10 (2H, s, PhH).

Poly (2,5-di-hexyloxy-1,4-phenylene-co-1,4-phenylene) (42)

A mixture of (39) (0.6 mmol) and (41) (0.3 mmol) was
polymerised in an identical fashion as (41) to yield a
brown solid((130 mg, 61 %); υ_{max} (KBr, cm^{-1}) 2920 (C-H),
1420 (Ph), 1200 (Ph-O), 1050 (C-O), 810 (Ph); δ_H (400
MHz, CDCl$_3$) 0.88 (6H, d, J 6.1, Me), 1.31 (8H, s, 1.42 (4H,
s), 1.74 (4H, s), 3.97 (4H, M, J 6.8), 7.10 (4H, d, J 6.7,
Ph), 7.75 (1H, s, Ph), 7.78 (1H, s, Ph).

Preparation of EL devices

A) A solution of (41) (4 mg) and polystyrene (36 mg) in 1
ml of chloroform was prepared. Spin-coating at 2000 r.p.m.
gave films of 300 nm. Blue emission was observed in an ITO
/ blend / calcium device. The internal quantum efficiency
was 1.2 % at a driving voltage of 90 V.

B) A solution of (41) (8 mg) and polystyrene (32 mg) in 2
ml of chloroform was prepared. Spin-coating at 2000 r.p.m.
gave films of 80 nm. Blue-green emission was observed in an
ITO / PPV/ polymer blend / calcium device. The internal
quantum efficiency was 0.15 % at a driving voltage of 50 V.

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C) A solution of (42) (22 mg) and oxadiazole (43) (22 mg) in 1.5 ml of chloroform was prepared. Spin-coating at 2000 r.p.m. gave films of 180 nm. Blue emission was observed in an ITO / polymer blend / calcium device. The internal quantum efficiency was 0.005 % at a driving voltage of 10 V.

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CLAIMS:

1.   An   electroluminescent   device   incorporating   an
emissive layer comprising a processible polymer matrix and
a   chromophoric   component,   wherein   the   chromophoric
component is blended with the polymer matrix or covalently
attached thereto as a side chain and is selected to emit
radiation in the region 400nm to 500nm when excited to
luminesce.

2.   An electroluminescent device according to claim 1,
wherein the chromophoric component is selected to emit
radiation in the region 430nm to 480nm.

3.   An electroluminescent device according to claim 1
or claim 2, wherein the chromophoric component has the
general   formula Ar_1-Ar_2 or Ar_1-Ar_2-Ar_3 in   which
Ar_1, Ar_2 and Ar_3 are   the   same   or   different   and
represent aromatic groups which are conjugatively linked
together.

4.   An electroluminescent device according to claim 3,
wherein the chromophoric component is asymmetric.

5.   An electroluminescent device according to claim 3
or claim 4, wherein the aromatic groups are linked to each
other by a double bond in trans conformation.

6.   An electroluminescent device according to any one
of claims 3 to 5, wherein at least one of the aromatic
groups is substituted with a ring substituent.

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7.   An electroluminescent device according to claim 6,
wherein the ring substituent comprises a solubilizing
group.

8.   An electroluminescent device according to any one
of claims 3 to 7, wherein the chromophoric component
comprises a stilbene or a distyrylbenzene.

9.   An electroluminescent device according to any one
of the preceding claims, wherein the chromophoric
component is covalently attached to the polymer matrix by
a non-conjugated spacer comprising a carbon chain of at
least two carbon atoms.

10.   An electroluminescent device according to any one
of the preceding claims, wherein the polymer matrix
comprises poly(methylmethacrylate).

11.   An electroluminescent device according to any one
of claims 1 to 8, wherein the chromophoric component forms
at least a part of a chromophoric polymer and is blended
with the polymer matrix.

12.   An electroluminescent device according to claim
11, wherein the chromophoric polymer comprises a
poly(paraphenylene).

13.   An electroluminescent device according to claim
12, wherein the poly(paraphenylene) has the general
formula (A):

(A)
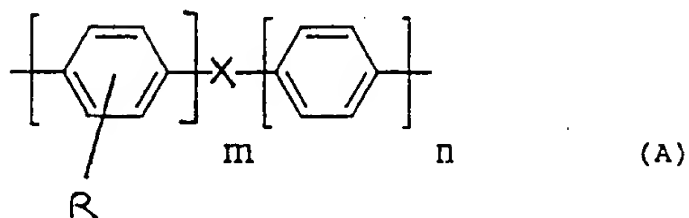
in which m is an integer and n is an integer or zero; R
represents up to four solubilizing groups; and X is
optionally a non-conjugated spacer group.

14.   An electroluminescent device according to claim
13, wherein the poly(paraphenylene) has the general
formula (B):

(B)
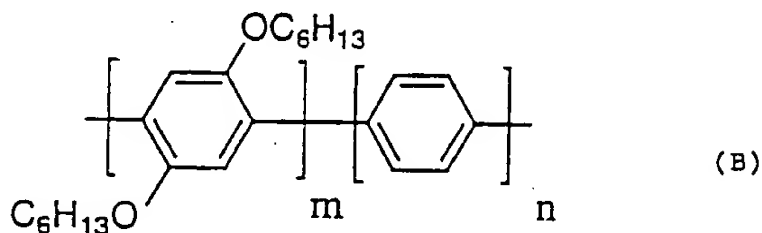
in which m is an integer and n=0, or m:n = 2:1.

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15.   An electroluminescent device according to any one
of claims 1 to 8 or 11 to 14, wherein the polymer matrix
comprises   poly(methylmethacrylate),   polycarbonate   or
polystyrene.

16.   An electroluminescent device incorporating   an
emissive layer comprising a processible polymer matrix and
a chromophoric component, in which the chromophoric
component is in the main chain of the polymer matrix and
is selected to emit radiation in the region 400nm to 500nm
when   excited   to   luminesce,   wherein   the   chromophoric
component comprises a stilbene or distyrylbenzene moiety.

17.   An electroluminescent device incorporating   an
emissive layer comprising a processible polymer comprising
a polymeric chromophoric component of general formula (A)
or (B) as defined in claim 13 or claim 14, wherein the
polymeric chromophoric component is selected to emit
radiation in the region 400nm to 500nm when excited to
luminesce.

Fig.1.

Fig.2

Fig.3

Fig.4.

ABSORBANCE OF POLYMER (23) ——————

ABSORBANCE OF COMPOUND (8) ——⊖——

ENERGY (eV)

Fig.5.

Fig.6

Fig.7.

Fig.8

Fig.9

Fig.10

Fig.11

Fig.12

Fig.13

NM	+1.900	ABSORBANCE	-0.100

600.0

560.0

520.0

500.0   0.001   POS.
498.4   -0.001   NEG.

480.0

440.0

400.0

360.0

320.0   321.8   0.365   POS.

280.0   282.2   0.275   NEG.

229.5   0.910   POS.

225.0
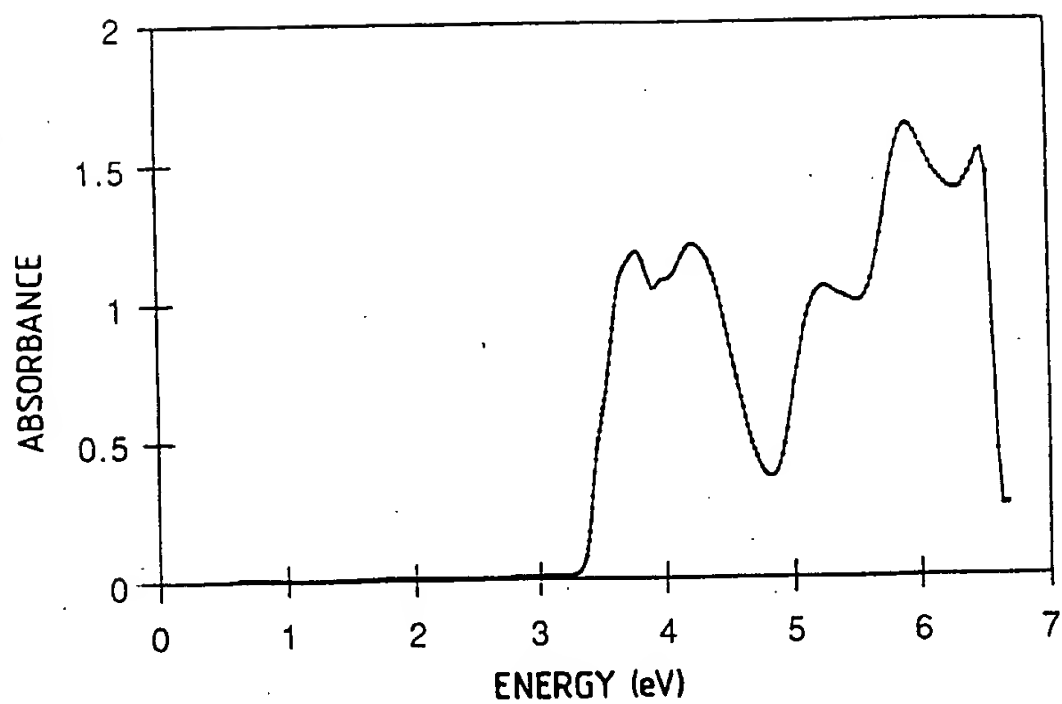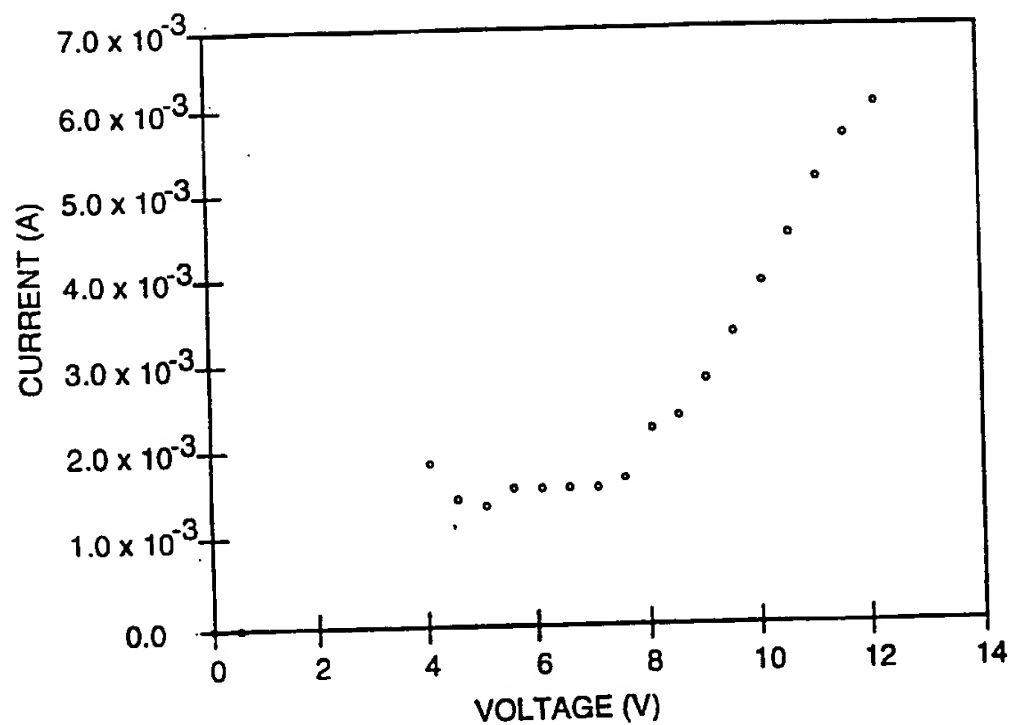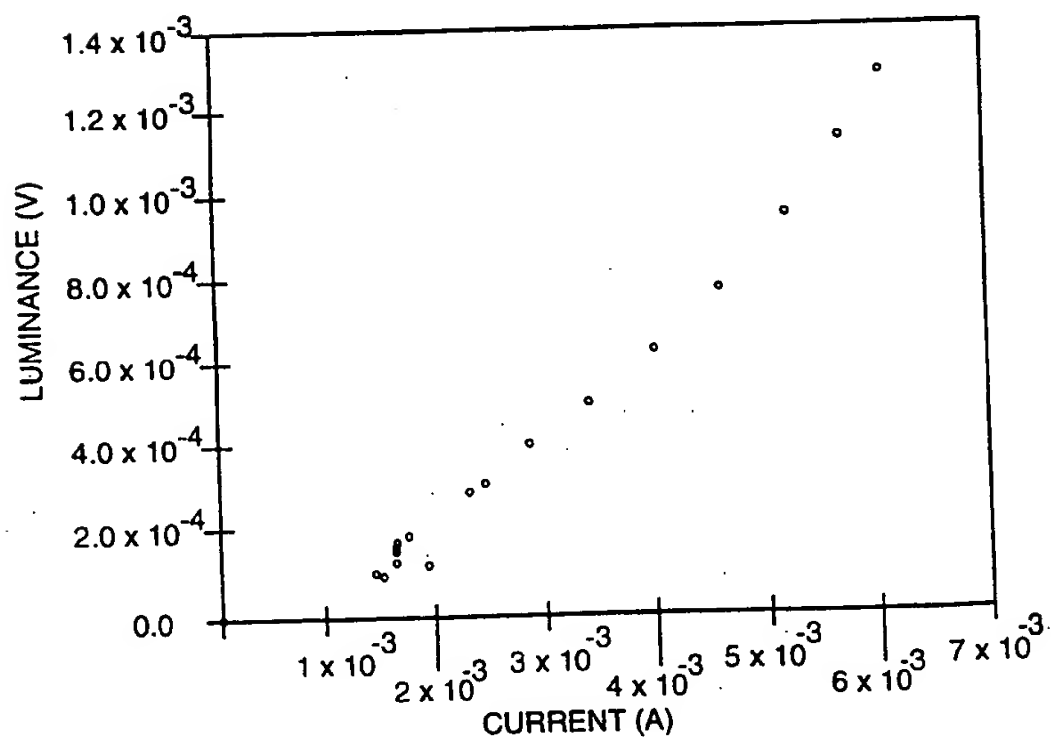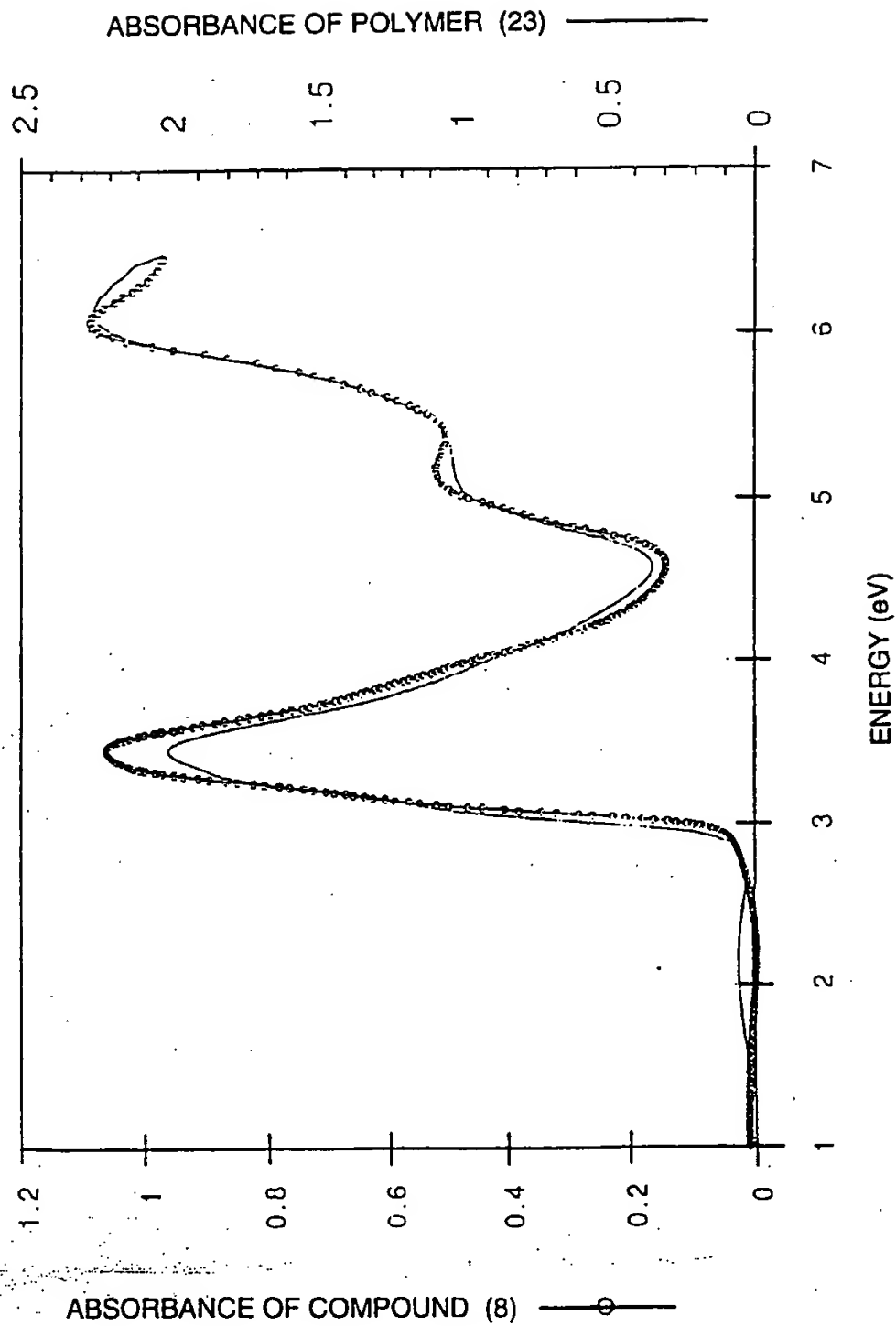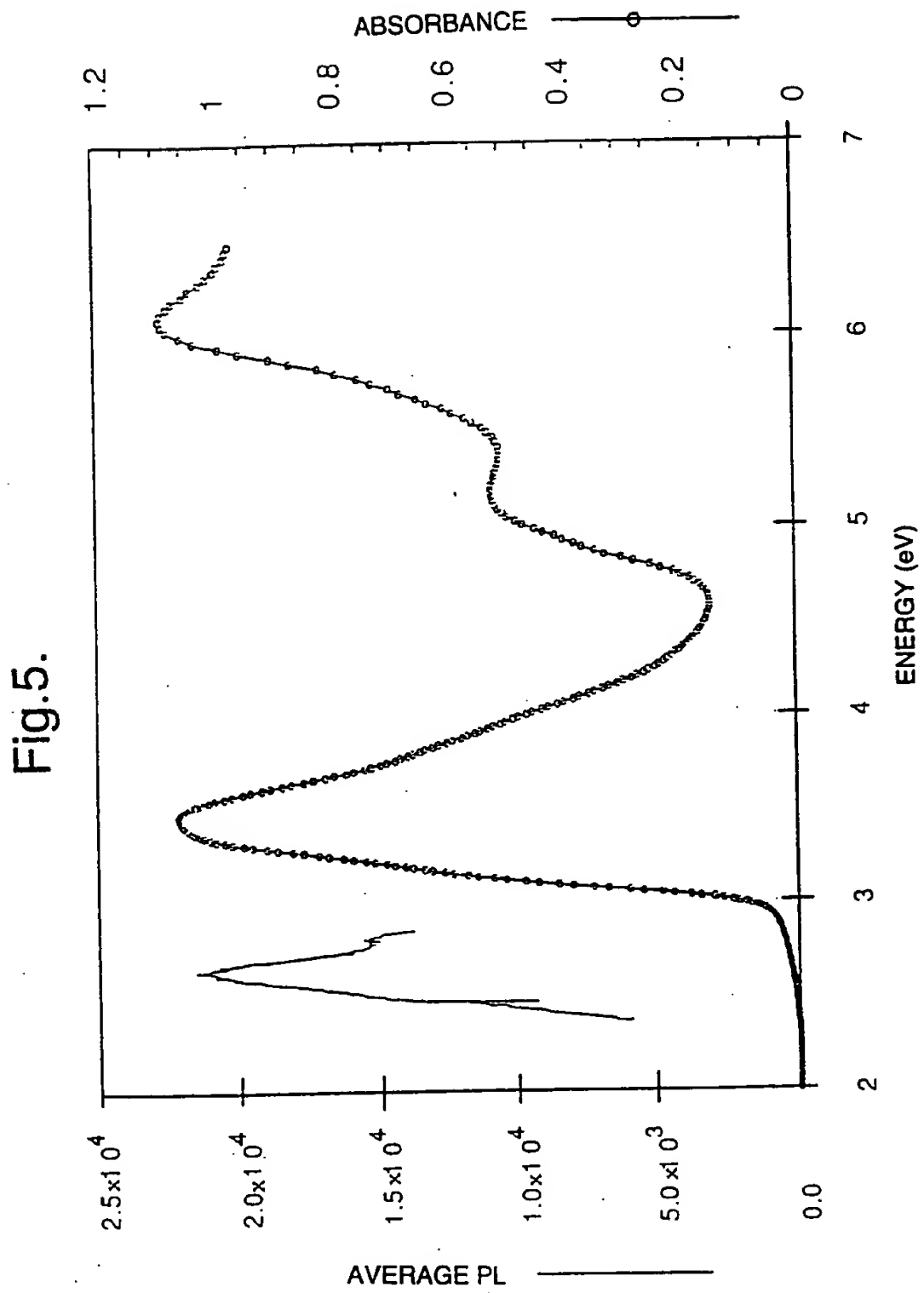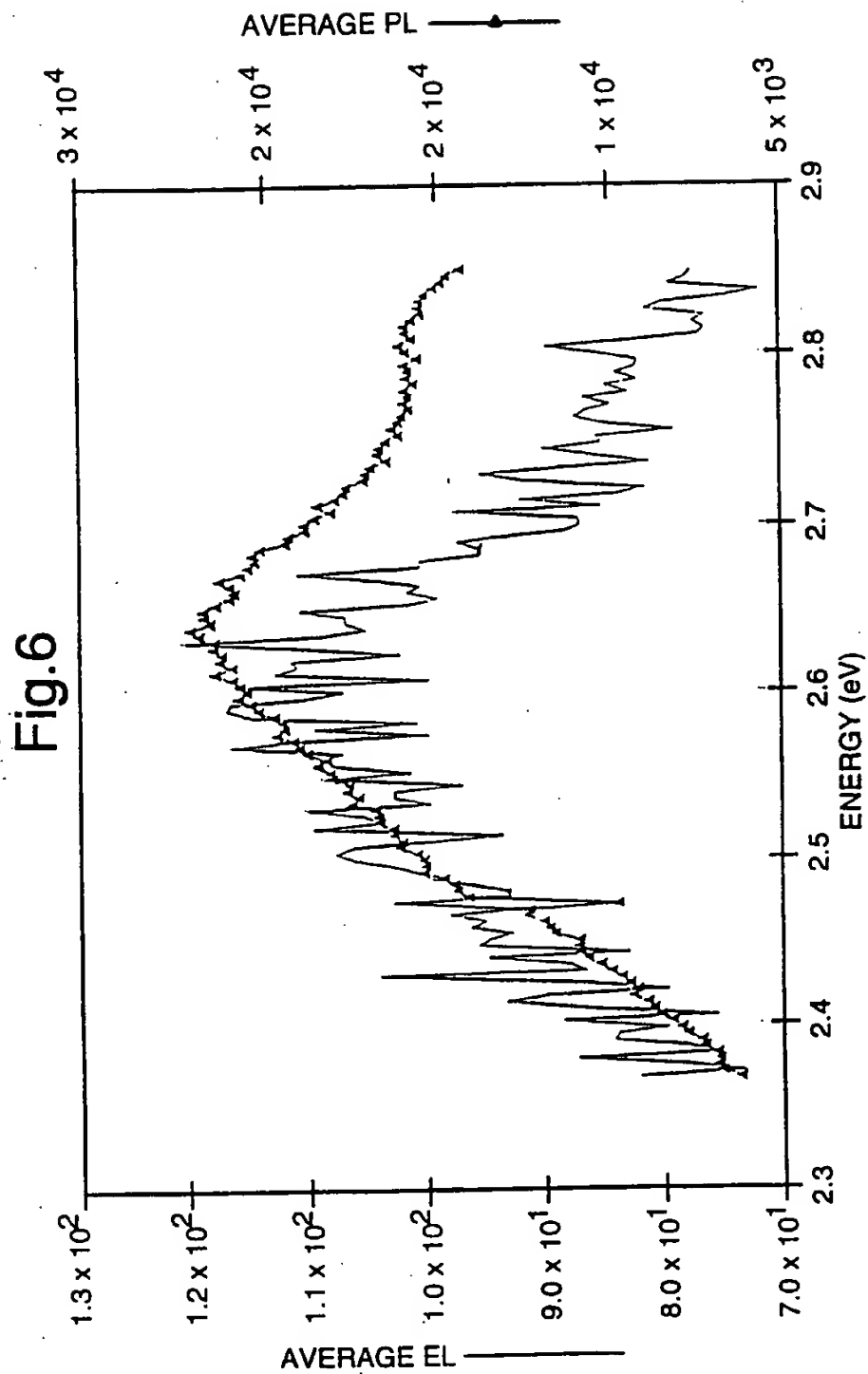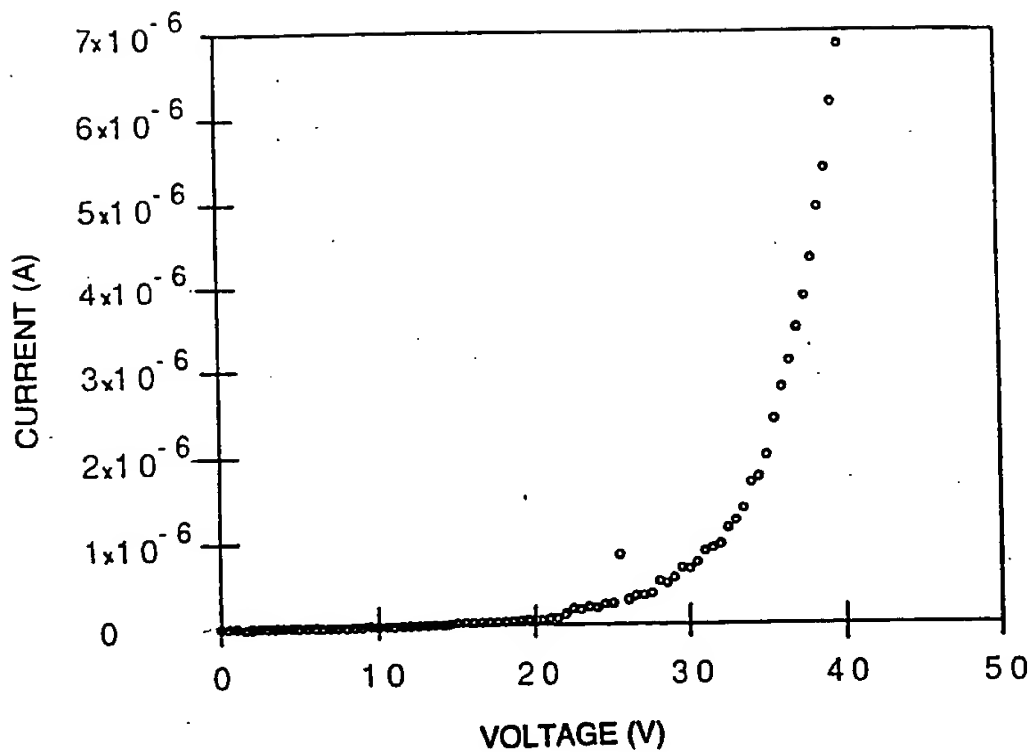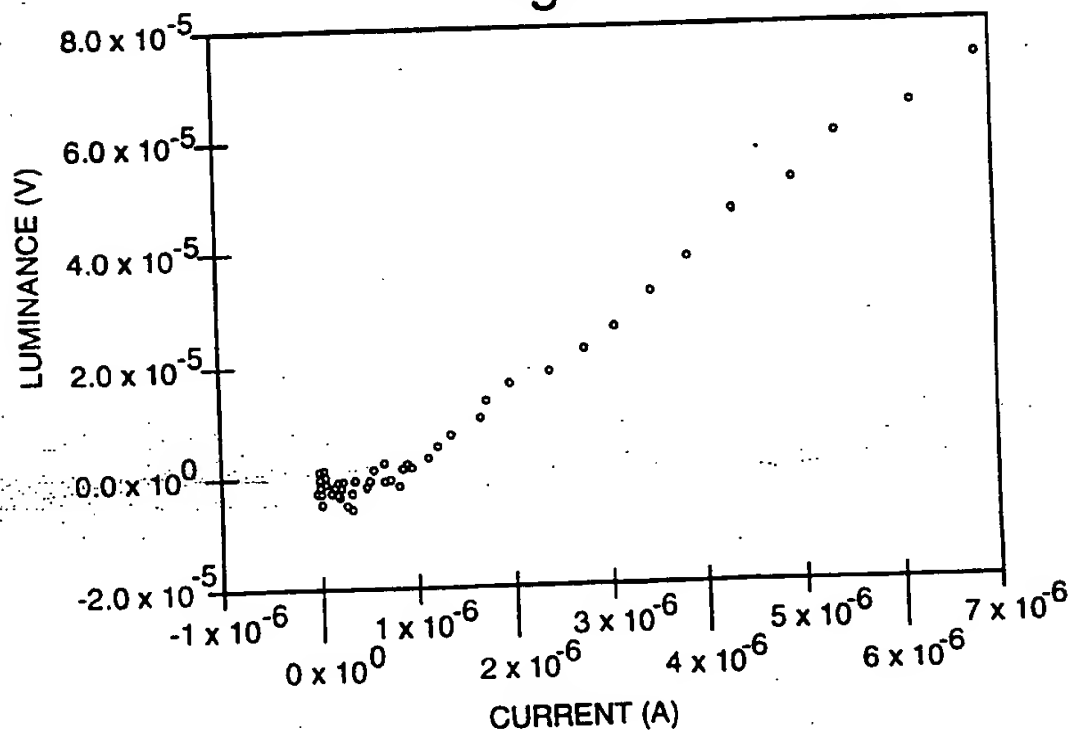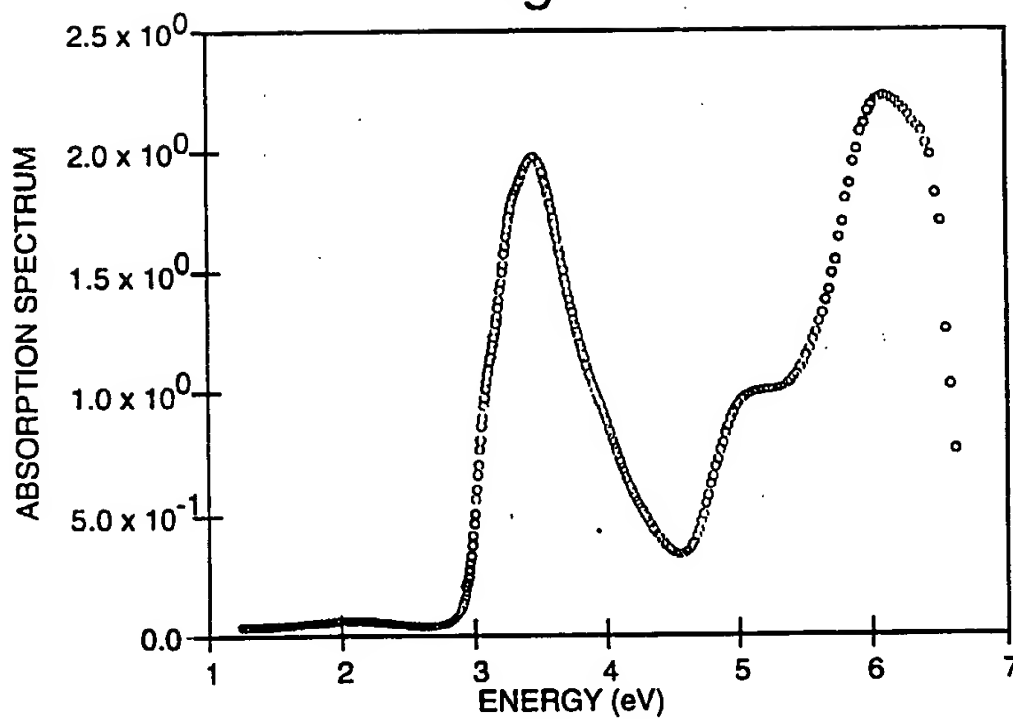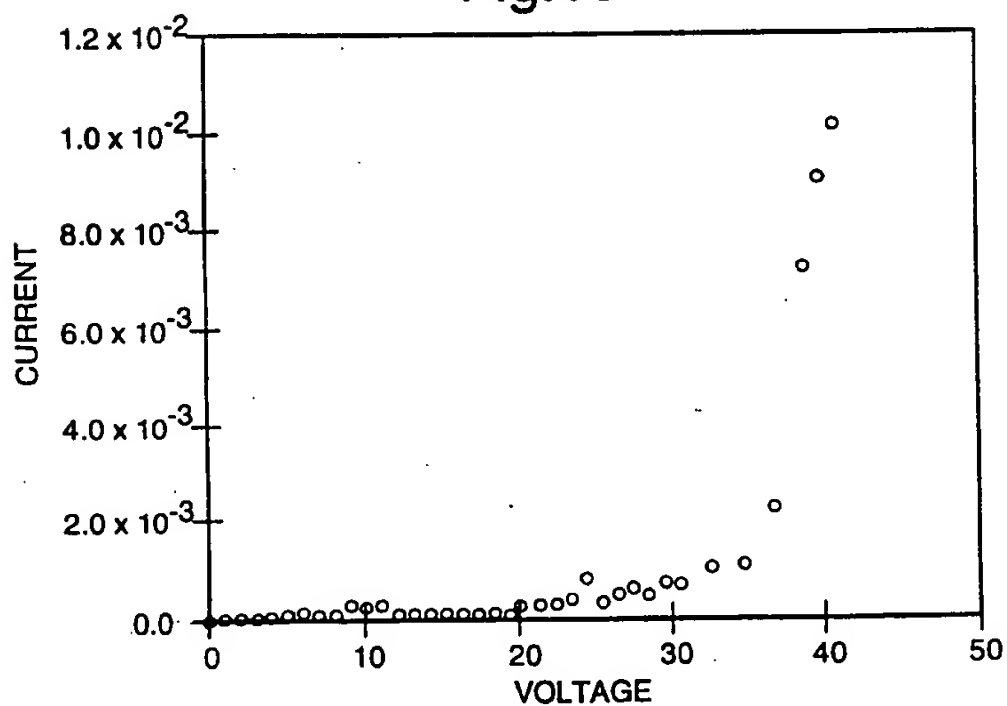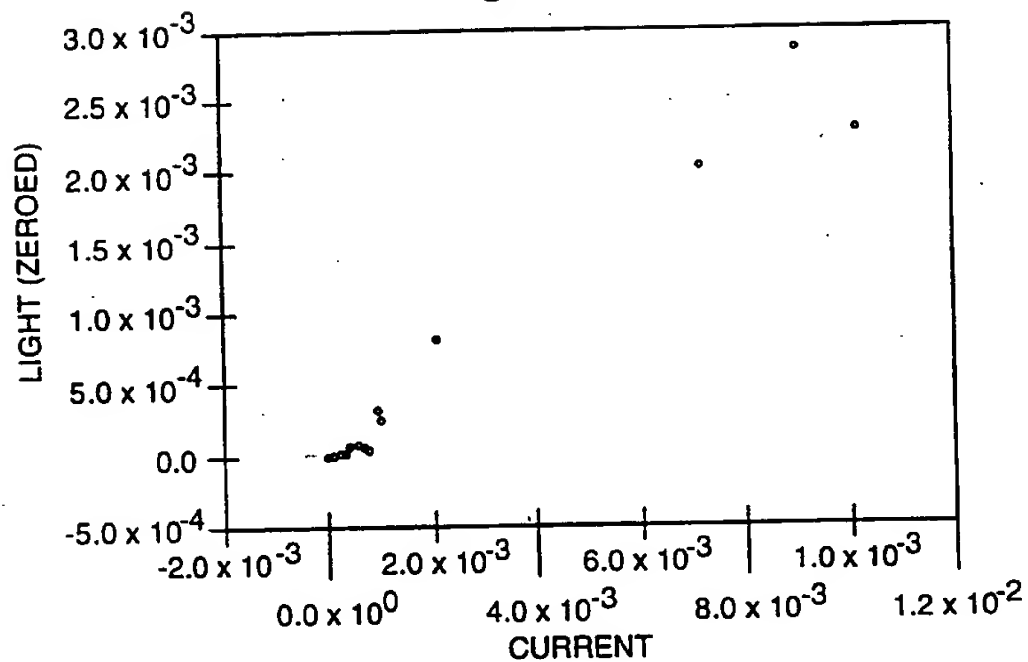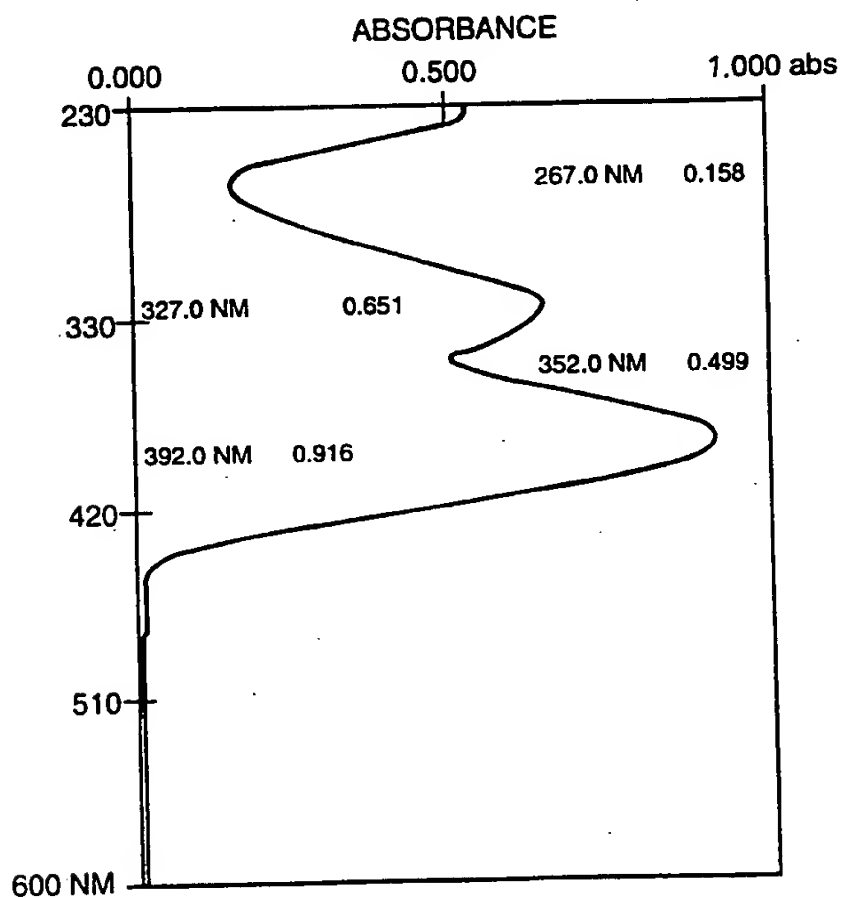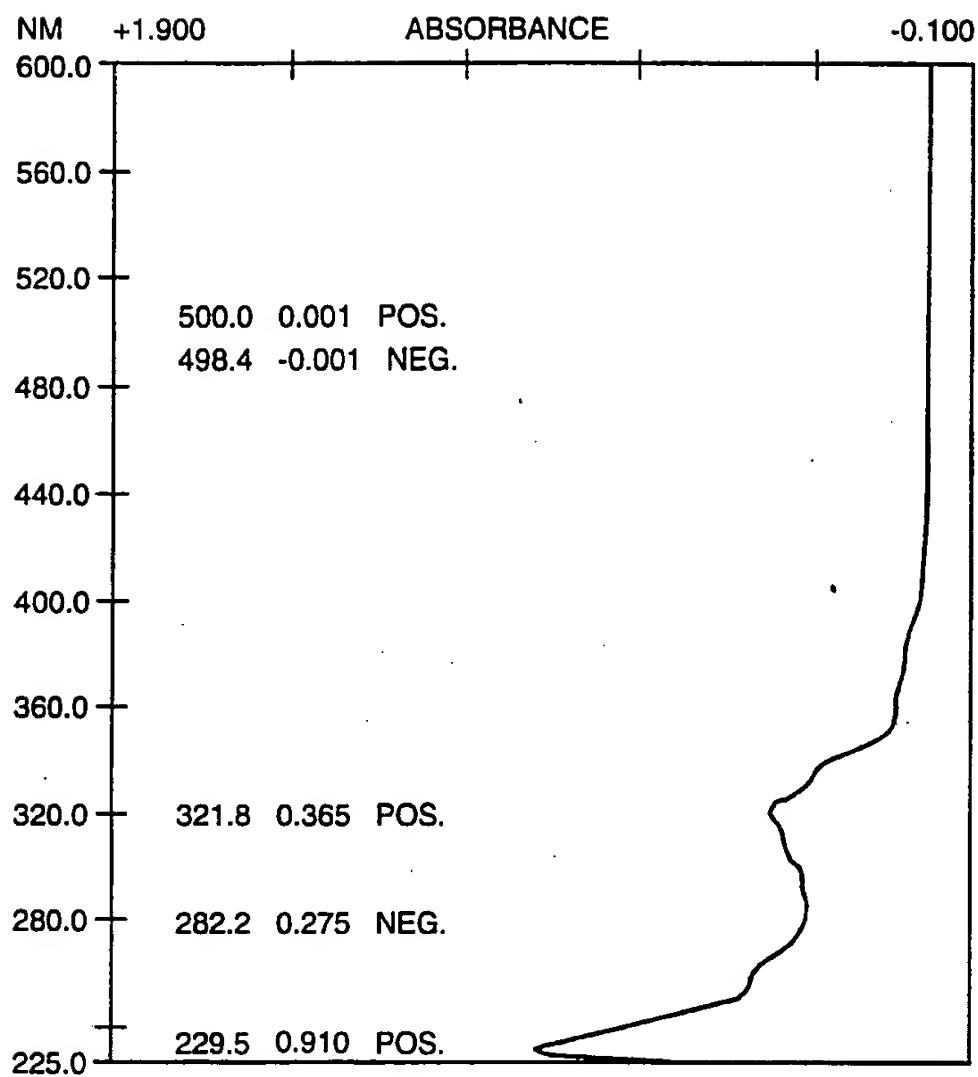
Fig.14.
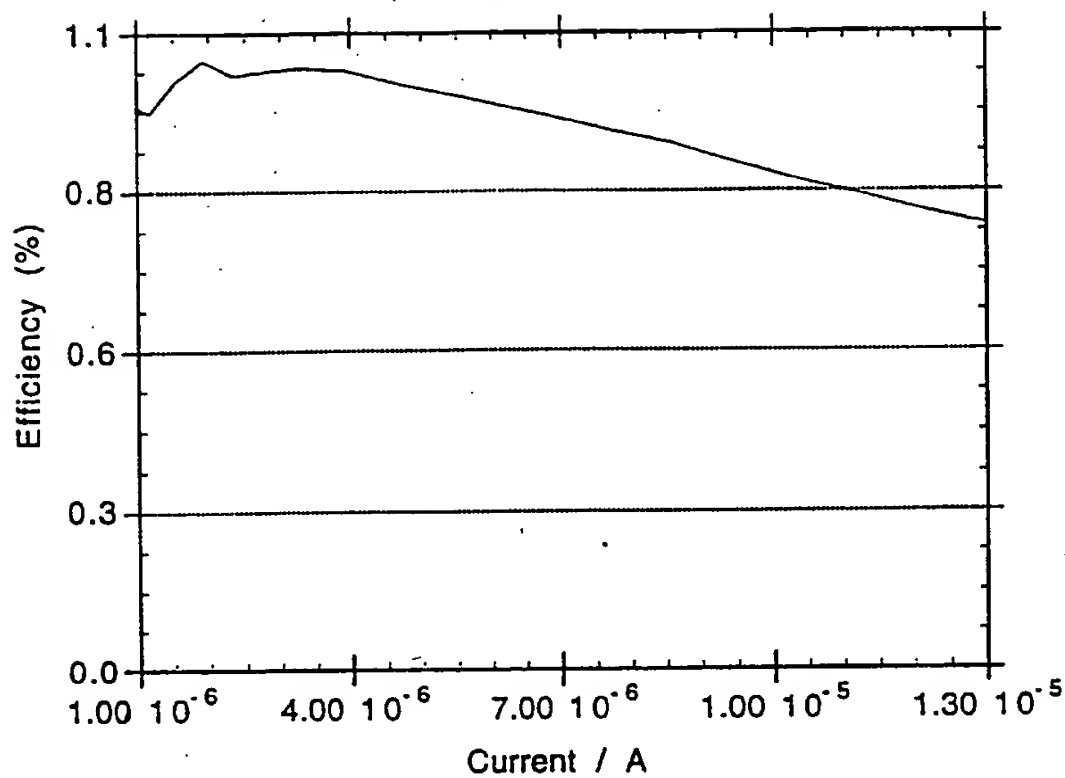
Fig.15.
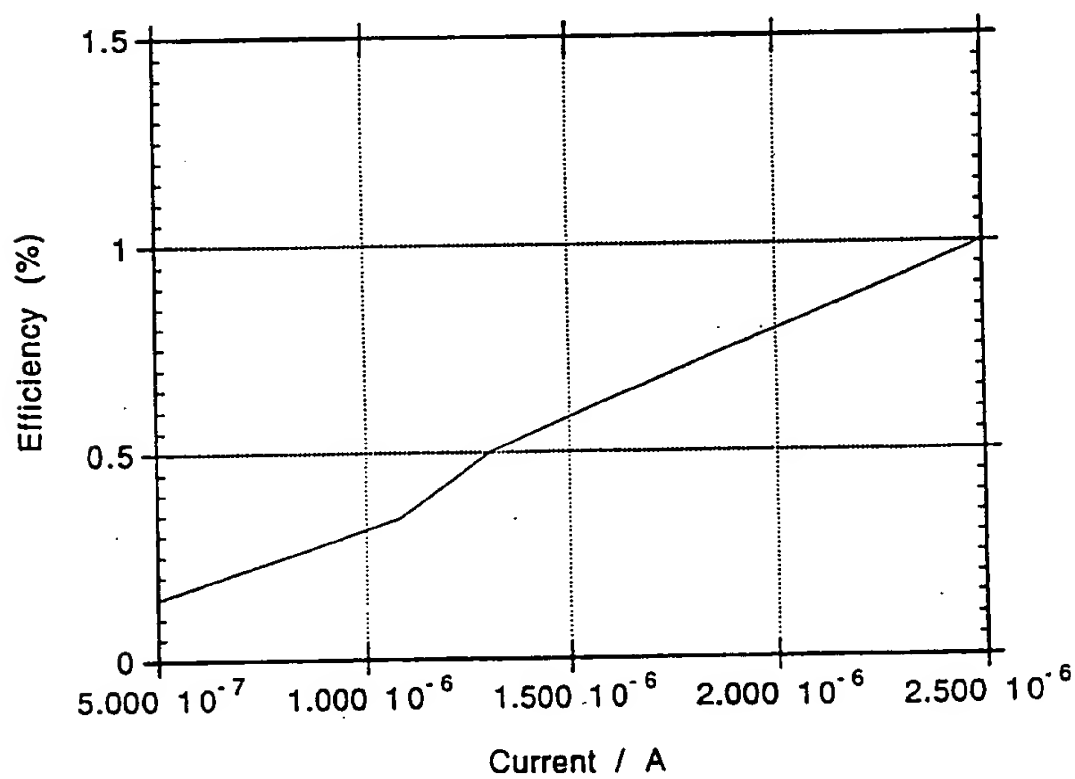
Fig.16.
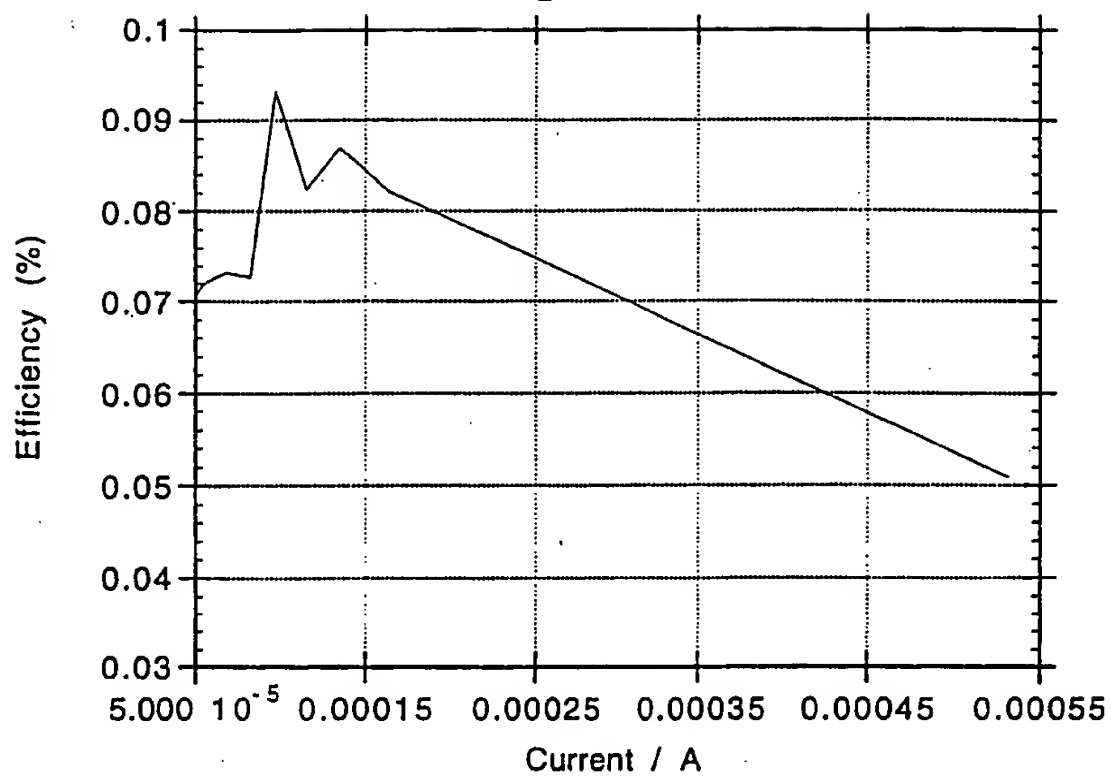
Fig.17.
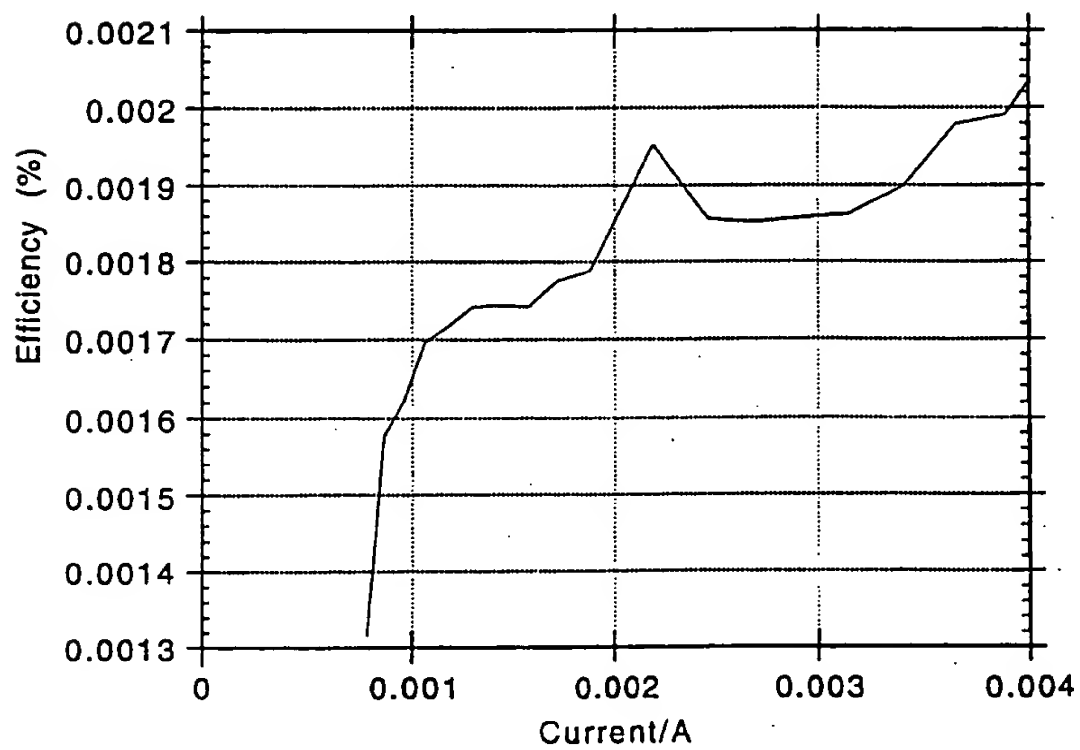
Fig.18.
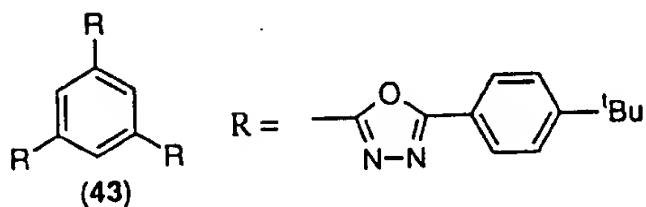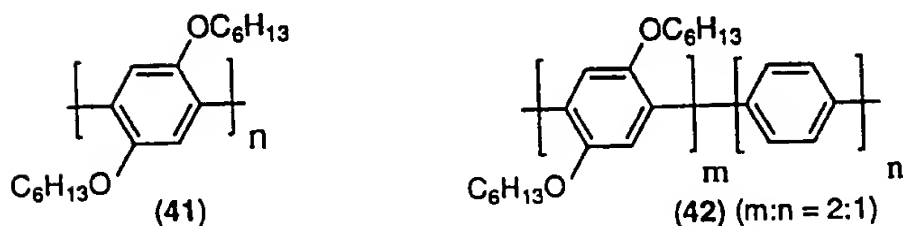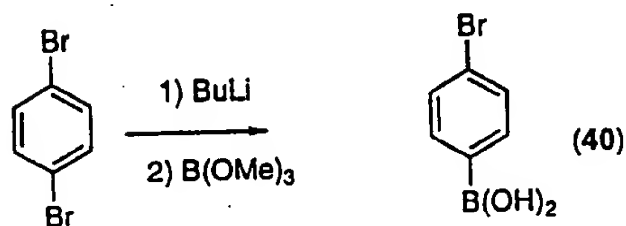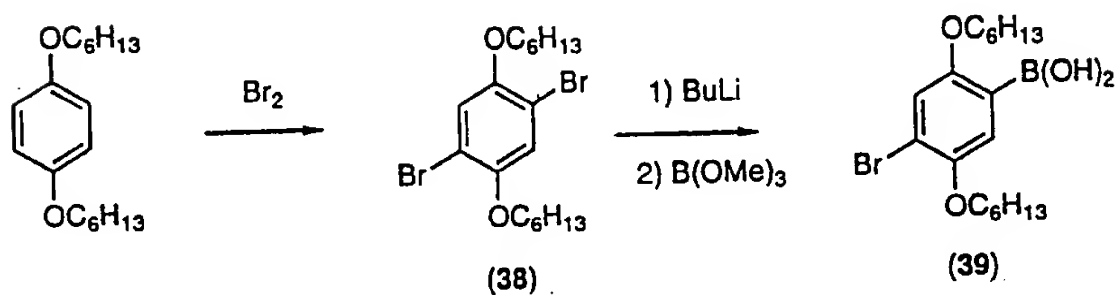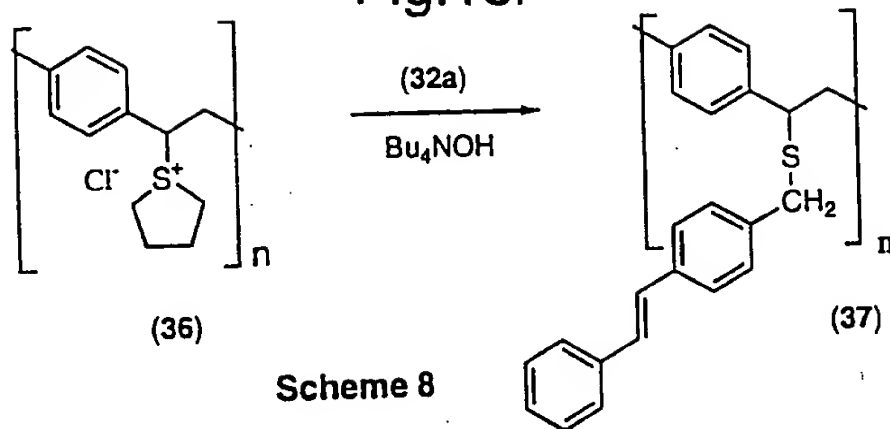
Scheme 8

Scheme 9

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: H05B 33/14, C09K 11/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C09K, H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent's abstract, No 86- 80870/12, week 8612, ABSTRACT OF SU, 1177318 (SAVOSKIN V M), 7 Sept 1985 (07.09.85)	1-17
A	Patent Abstracts of Japan, Vol 14, No 509, C-776, abstract of JP, A, 2-209988 (IDEMITSU KOSAN CO LTD), 21 August 1990 (21.08.90)	1-17
A	EP, A2, 0319881 (IDEMITSU KOSAN COMPANY LIMITED), 14 June 1989 (14.06.89), page 3, line 34 - line 38; page 4, line 49 - line 53; page 6, line 15 - line 17	1-17

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 March 1994	12. 04. 94

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	May Hallne Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/01/94

International application No.

PCT/GB 93/02586

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0319881	14/06/89	JP-A- 1254791	11/10/89
		US-A- 5121029	09/06/92
		JP-A- 1245087	29/09/89

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